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Ionization of Argon, Neon and Helium by A, Ne and He Atoms

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(Received February 6, 1933)

The ionization of argon, neon and helium under impact of A, Ne and He atoms was investigated by a method which eliminated errors due to secondary electrons. When argon, neon and helium were bombarded with their own atoms, ionization was found to set in at approximately 100 equivalent volts in each case. When any one of these three rare gases was bombarded with atoms of either of the other two, no ionization could be detected. If ionization had set in at 150 volts or less it should have been apparent.

PREVIOUS experiments[1] indicated that under impact of their own atoms, helium was ionized at 60 equivalent volts, neon at 50 volts and argon at 40 volts. A higher ionization potential was found in argon at 75 to 85 volts and in neon at 110 to 120 volts. These experimental results were open to criticism because of the presence of secondary electrons which could not be eliminated. The experiments described here were undertaken with an apparatus which eliminated complications due to secondary electrons, in an attempt to get unambiguous values of the energy required to ionize helium, neon and argon by their own atoms and also to study the ionization of each rare gas under impact of atoms of another.

The apparatus used is shown drawn to scale in Fig. 1. The experimental tube is divided into three parts: the discharge chamber (D.C.), the evacuated chamber (E.C.) and the ionization chamber (I.C.). A discharge was produced between the oxide coated filament F and the anode A. Positive ions of the gas are produced by electron impact and drift toward the filament. Since the voltage across the discharge, V_d, is concentrated at the filament, most of the positive ions that pass through the 1 mm hole in the plate P_1 will have an energy of V_d equivalent volts. Between P_1 and P_2 they are further accelerated by an applied potential V_a. P_2 is 1 cm from the end of D.C. and in this part of their path, at the pressures used, approximately 85 percent of the ions are neutralized, with little or no loss of energy, by exchange of charge with "resting" gas atoms. Consequently there emerges from the 1 mm orifice in the glass partition at the end of D.C., a beam composed mostly of neutral atoms of energy (V_d+V_a) equivalent volts. E.C. is kept

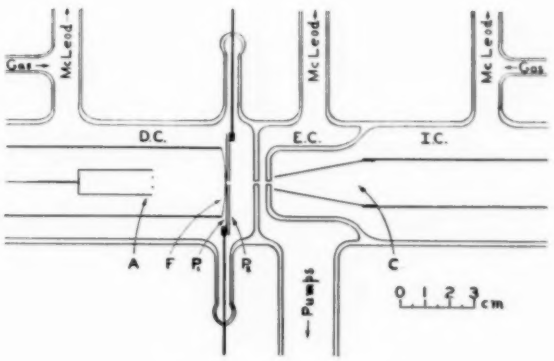

FIG. 1. Experimental tube.

[1] C. J. Brasefield, Phys. Rev. **42**, 11 (1932).

at a relatively low pressure by a diffusion pump. In E.C., the atomic beam passes between the plates of a small condenser (not shown in the diagram) to which a potential of 160 volts is applied. This removes from the beam most of the unneutralized positive ions, as well as any electrons which may have been carried with the beam in passing through the orifice at the end of D.C. The "purified" atomic beam now passes through a 1 mm orifice into I.C. where the atoms of the beam are free to collide with any gas atoms that may be present. The products of any resulting ionization are drawn to the plates of the condenser *C*. The galvanometer had a sensitivity of 10^{-11} amp. per mm. An applied potential of 15 volts was found to be sufficient to saturate the ionization current.

The gas of which the atomic beam was to be formed, and the gas to be bombarded were admitted to D.C. and I.C., respectively, by means of variable artificial leaks. Keeping V_d and I_d (the discharge current) constant, the accelerating potential V_a was varied up to 150 volts and readings were taken of the ionization current I_c. A test run was then taken under identical conditions except that the gas supply to I.C. was shut off and I.C. connected to the pumps. The ionization current during the test run, I_0, can be due only to those positive ions which succeed in passing the condenser in E.C. or to ionization of residual gas present during the test run or to secondary electrons from orifice between E.C. and I.C. That these effects are small is shown in Fig. 2 where I_0 for argon is also shown. The ratio of I_0 to I_c is about the same for Ne and He as for A. All nine combinations of A, Ne and He were investigated. Only when these gases were bombarded with their own atoms was positive evidence of ionization below 150 volts obtained.

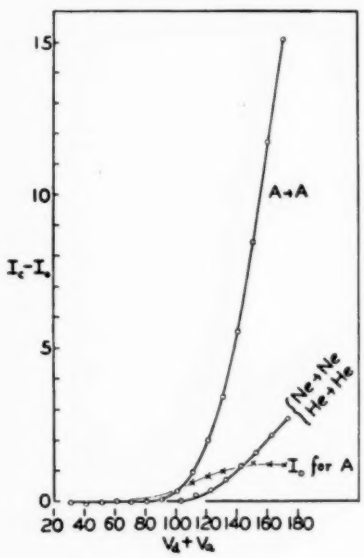

FIG. 2. Ionization of helium, neon and argon under impact of their own atoms.

RESULTS

Argon atoms bombarding argon (A→A)

Data: Pressure in D.C. $(P_d)=0.031$ mm; pressure in I.C. $(P_i)=0.041$ mm; pressure in E.C. $(P_e)=0.0046$ mm; pressure in E.C. and I.C. during test run $(P_0)=0.0022$ mm; $V_d=21$ volts; $I_d=42$ m.a. In Fig. 2 the net ionization current (I_c-I_0) in galvanometer deflection (cm) is plotted as a function of the energy of the impinging atoms in (V_d+V_a) equivalent volts. Ionization is observed to set in slightly under 100 volts, say at 90 volts.

Ne→Ne

Data: $P_d=0.047$ mm; $P_i=0.060$ mm; $P_e=0.0065$ mm; $P_0=0.0032$ mm; $V_d=42$ volts; $I_d=29$ m.a. Ionization is observed to set in slightly above 100 volts, say at 110 volts.

He→He

Data: $P_d=0.055$ mm; $P_i=0.065$ mm; $P_e=0.008$ mm; $P_0=0.0038$ mm; $V_d=64$ volts; $I_d=14$ m.a. It so happens that the observed values of (I_c-I_0) are practically identical for both Ne→Ne and He→He. Ionization is observed to set in slightly above 100 volts, say at 110 volts.

A→Ne, A→He; Ne→A, Ne→He; He→Ne, He→A

In none of these cases could any ionization be detected. Since the energy of the impinging atoms ranged as high as 200 volts, any ionization setting in at 150 volts or less would have been observed, provided that the probability of ionization was of the same order of magnitude as for A→A, Ne→Ne or He→He.

These results indicate that the minimum ionization potentials of the rare gases under impact of their own atoms, reported previously,[1] were

spurious, and were due to the presence of secondary electrons. What were reported previously as higher ionization potentials were really the minimum ionization potentials and are in quite good agreement with the values given here. As a matter of fact, if complications due to secondary electrons are considered, even the values first reported [2] (which were later abandoned as unreliable) are not in bad agreement with the most recent results.

Similar experiments have been reported by Beeck.[3] He finds that neon is ionized by argon atoms and also that argon is ionized by its own atoms at energies as low as 60 equivalent volts, no minimum ionization potential being indicated in either case. The experiments here reported do not confirm any of these findings.

From considerations of conservation of energy and momentum, we might expect the rare gases to be ionized under central impacts of their own atoms as follows: A→A at 31 volts, Ne→Ne at 43 volts and He→He at 49 volts. It is evident, therefore, that an explanation of the higher values here reported must be found in some other theory, possibly along the lines suggested by Weizel and Beeck,[4] namely, that a pseudomolecule may be formed as a result of the collision of two atoms and that on dissociation one of the components may find itself ionized as a result of the Auger effect.

[2] C. J. Brasefield, Phys. Rev. **41**, 394 (1932).

[3] O. Beeck, Zeits. f. Physik **76**, 799 (1932); Proc. Nat. Acad. Sci. **18**, 311 (1932).

[4] W. Weizel and O. Beeck, Zeits. f. Physik **76**, 250 (1932).

This experiment yields no values for the efficiency of ionization of the rare gases under impact of their own atoms.[5] For the purposes of this experiment it is quite sufficient to know that the number of impinging atoms remains constant. The number of impinging atoms should be approximately proportional to the positive ion current I_a between the plates P_1 and P_2. I_a does not remain constant but increases gradually with V_a—not rapidly enough, however, to affect the results as given. For if $(I_e-I_0)/I_a$ is plotted against (V_d+V_a), the slopes of the curves are slightly less than those shown in Fig. 2, but the apparent intercept remains unchanged.

More satisfactory ionization curves than those shown in Fig. 2 (and consequently more accurate values of the ionization potentials) could probably be obtained by using an atomic beam of more nearly homogeneous velocity. This would require a magnetic selection of the positive ions passing through the hole in P_1. It is doubtful whether the increased experimental difficulties would justify an attempt to improve the present results, until further advances from the theoretical side demand it.

[5] The curves given in Fig. 4, Phys. Rev. **42**, 16 (1932) must be corrected because of the error due to secondary electrons. The A^0 and Ne^0 curves may be approximately corrected by multiplying the ordinate by a factor 0.4. The correction to be applied to the He^0 curve is unknown. The A^+ curve should be correct as given. The corrected values for the efficiency of ionization of A and Ne under impact of A and Ne atoms, respectively, are in the neighborhood of the values given by Sutton and Beeck for the efficiency of ionization of A and Ne by K^+ and Na^+, respectively.

The Action of Mercury Metastable Atoms on a Tungsten Surface

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(Received March 23, 1933)

The electron emission from metal surfaces due to the action of the 2^3P_0 metastable atoms was studied under varying conditions. The metastable atoms were produced by electron impact and diffused to the surface. The sensitivity of any metal surface was found to vary markedly with the vacuum conditions in the experimental tube and the extent to which the surface had been cleaned and outgassed. After thorough outgassing and cleaning each of the metals tested acquired practically the same sensitivity, which furthermore for any metal remained very nearly constant over long periods. Heating of a surface after it had acquired this equilibrium or "normal" sensitivity always resulted in temporary changes of the sensitivity following which it returned to its normal value. Investigation of these temporary changes of the sensitivity for a tungsten surface, with different mercury vapor pressures, showed that a deposit of mercury atoms was essential for the formation of a surface sensitive to mercury metastable atoms. The nature of these changes further indicated that the residual gas (oxygen) also played an important part and that the normal value of the sensitivity was due to the establishment of a very stable, complex arrangement of mercury and oxygen atoms upon the tungsten. Carefully dried oxygen was admitted to the experimental tube, and the observations of the changes in sensitivity as this oxygen was removed by progressive outgassing confirmed the conclusions as to the part played by oxygen. Transient values of the sensitivity fifty to a hundred times larger than the normal value were observed at one stage of this outgassing process when the relative concentrations of oxygen and mercury atoms were such as to make possible the formation of monatomic films. From the values of these high sensitivities it is concluded that in the case of the normal surface not more than one or two metastable atoms out of a hundred caused the emission of an electron. The formation of the sensitive surface was found to be uninfluenced by the metastable atoms. No correlation was found between the changes of response of a surface to mercury metastable atoms and to the radiation from an external source.

INTRODUCTION

ELECTRON emission by metal surfaces as the result of impact by metastable atoms has been investigated in some detail in the case of mercury and the rare gases. Webb,[1] Messenger[2] and Coulliette,[3] have studied the action of mercury metastable atoms on nickel surfaces. Oliphant[4] found that a large emission of electrons resulted from the impact of metastable helium atoms on metals. Uyterhoeven and Harrington[5] and others have obtained large electron emissions from cold electrodes in discharges of neon, argon and helium, which they explained as due in part to the action of long lived metastable atoms. Work of similar nature in neon has been reported by Langmuir and Found.[6] On the other hand, Kenty[7] attributes a large part of this electron emission in neon to abnormal photoelectric effect or to ionization of traces of foreign gas by the metastable atoms. In the case of mercury the energy of the metastable atom is too small to produce any ionization and Messenger has shown by the use of calcite and quartz windows, which could be interposed at will between the source of the metastable mercury atoms and the metal plate used as a detector, that in the usual type of Lenard tube used to measure critical potentials the greater part of the emission from the metal plate was due to the direct action of the metastable atoms, and that the ordinary photoelectric emission due to radiation excited in the tube was only a few percent of this. This was somewhat surprising in view of the fact that the energy available in the 2^3P_0 state (which is the longer lived metastable state and therefore the more

[1] H. W. Webb, Phys. Rev. **24**, 113 (1924).
[2] H. A. Messenger, Phys. Rev. **28**, 962 (1926).
[3] H. J. Coulliette, Phys. Rev. **32**, 636 (1928).
[4] M. L. E. Oliphant, Proc. Roy. Soc. **A124**, 228 (1929).
[5] W. Uyterhoeven and M. C. Harrington, Phys. Rev. **35**, 438 (1930) and Phys. Rev. **36**, 709 (1930).
[6] C. Found, Phys. Rev. **34**, 1625 (1929); I. Langmuir and C. Found, Phys. Rev. **36**, 604 (1930); C. Found and I. Langmuir, Phys. Rev. **39**, 237 (1930).
[7] C. Kenty, Phys. Rev. **38**, 377 (1931); Phys. Rev. **43**, 181 (1933).

important) is only 4.68 electron-volts, which is very close to the work function of the metals used, while the two most important lines excited corresponded to 4.86 and 6.7 volts, respectively. This fact and the observations on the variations in the sensitivity to the action of the metastable atoms resulting from changes of temperature, of mercury vapor pressure, and of the amount of residual gas suggested the present investigation, the object of which was to determine something of the nature of the action and the factors upon which it depended.

Preliminary Tests

The experimental tubes used were four electrode tubes with an oxide coated cathode, and a grid to produce and accelerate electrons which by impact excited mercury atoms to the 2^3P_0 metastable state. These atoms diffused to the metal surface under investigation from which they caused emission of electrons which were drawn off by a second grid maintained at a suitable potential. The first significant experiments were made with a tube having no greased or waxed joints, since earlier work had shown that the vapors from such joints caused marked variations in the response of the surface both to light and to mercury metastable atoms. This tube was provided with a side arm into which the surface under test was withdrawn and thoroughly cleaned and outgassed so that the main portion of the tube where measurements were made could be kept free from contamination. The surface could be either illuminated by monochromatic light through a quartz window or subjected to the action of the metastable atoms, in order to compare these two causes of electron emission.

To determine what part of the response was due to metastable atoms and what part was due to photoelectric action of the radiation from the hot cathode and of the radiation excited by electron impact in the vapor, a sliding quartz window was moved magnetically in front of the surface screening it from metastable atoms and permitting only the radiation to reach the surface. In this way it was determined that for every metal used only one or two percent of the total response was due to such radiation.

Surfaces of tungsten, nickel, iron, platinum, molybdenum and tantalum were mounted successively in this tube and tested both for response to mercury metastable atoms and to monochromatic light from an external source. For the latter purpose $\lambda 2650$ isolated from a mercury arc by a quartz monochromator was used since the energy per quantum of this radiation is very nearly the same as the energy of the mercury 2^3P_0 state. In addition measurements of the photoelectric response to the shorter wavelengths $\lambda 2537$ from a mercury arc $\lambda 2140$ from a zinc spark were made. While the response both to light and to metastable atoms varied markedly with vacuum conditions and with previous heat treatment of the surface, no correlation whatsoever was found between the changes in response to the action of metastable atoms and changes in response to the radiation of any of the wavelengths used. For example, a twenty-fold variation in the photoelectric effect was obtained under conditions which produced no appreciable change in the response to metastable atoms; under other conditions when marked increases in the response to metastable atoms were obtained, the photoelectric response diminished.

After prolonged heat treatment and outgassing of a given surface its response to metastable atoms became very nearly constant; i.e., while large changes followed any heat treatment of the surface, its response always returned to a value which did not vary more than ten percent from day to day. Furthermore, this value was very nearly the same for all of the metal surfaces tested. This result suggested that the response of the metal surface might in every case be due to a common impurity rather than to the metal itself. Accordingly a more thorough investigation was made of the effect of the residual gas and mercury vapor upon the response of a surface to mercury metastable atoms.

Apparatus

Since the best possible vacuum conditions are essential for such investigations, large experimental tubes containing magnetically operated shutters with their inevitable large masses of metal could not be used. A smaller and much simpler tube was therefore constructed with a minimum amount of metal. This tube is shown in Fig. 1. It contains an excitation system, having as

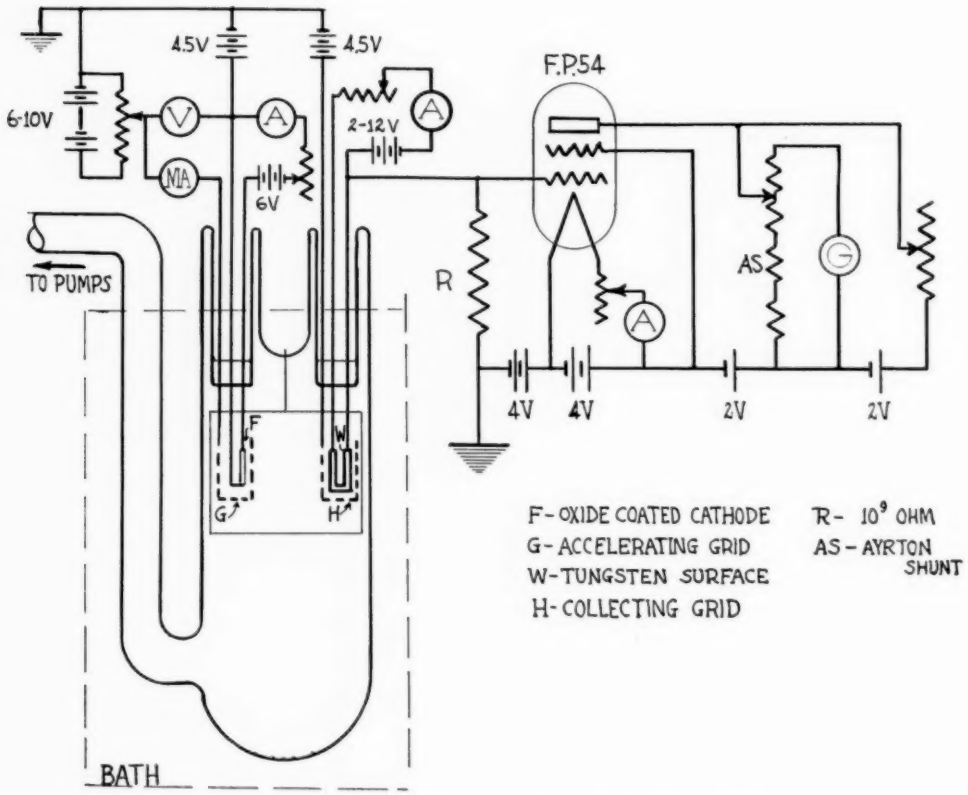

FIG. 1. Diagram of experimental tube and electrical circuits.

a source of electrons an oxide coated platinum cathode, *F*, surrounded by an accelerating grid of nickel, *G*, and a detecting system consisting of the surface studied, *W*, surrounded by a collecting nickel grid, *H*.

The surface *W* was made of tungsten foil, one mil thick in the shape of a "⊔" so that it could be heated for outgassing and subsequent heat treatment. This "⊔" was 10 mm long and 4 mm wide, the tungsten strip itself being one mm wide. A punch and die were used to cut this surface uniformly after several surfaces cut by hand had been burnt out during the outgassing process, apparently because of irregularities in the cutting.

The pumping system consisted of a mercury diffusion pump and a mechanical forepump, the residual gas pressures being measured by means of a McLeod gauge. Between the experimental tube and the pumping system was a magnetically operated mercury cut-off. To procure the best possible vacuum conditions the usual precautions of modern high vacuum technique were observed. No wax or greased joints of any kind were used, and the only stopcocks were on the fore vacuum side of the diffusion pump. Outgassed metal was used in the construction of all of the electrodes, which after fabrication were outgassed again before being put into the experimental tube. The mercury for the diffusion pump, McLeod gauge, and the cut-off was distilled into the system in as good a vacuum as possible. The tube itself was baked for many hours at about 500°C and the pumping tube flamed during this process.

The tungsten surface *W*, was heated by currents from a storage battery which was carefully insulated and shielded so that electron emission currents due to metastable atoms could be measured while the surface was being heated. This was possible up to temperatures of approximately 1000°K above which thermionic emission masked electron emission produced by the metastable atoms. The higher temperatures of the surface reached during outgassing and heat treatment

were measured by means of a disappearing filament type optical pyrometer while temperatures below the range of this instrument were measured by means of a small thermocouple welded to an identical surface in a duplicate tube.

To measure the electron currents produced by the action of metastable mercury atoms on the tungsten surface, which were of the order of 10^{-12} and 10^{-13} ampere, the surface was connected to a vacuum tube electrometer (FP–54) the changes in the plate current of which were measured by means of a galvanometer (sensitivity 10^{-10} ampere/millimeter) which was provided with a universal shunt.[8] With this method of measuring the electron current rapid changes in the response were readily followed. The circuits used are shown in Fig. 1.

The mercury vapor pressure was controlled by immersing the lower part of the tube as well as part of the pumping tube in a constant temperature bath. By occasional baking of the tube the amount of liquid mercury in it was restricted to a few small drops so that the mercury vapor pressure could be changed very rapidly. To measure the residual gas pressure the tube itself was used as an ionization manometer by using the hot-cathode and the two grids. This was calibrated against the McLeod gauge which was then sealed off. During the measurements of the residual gas pressure the tube was immersed in liquid air to remove the mercury vapor.

After the removal of the McLeod gauge the tube was again baked at 500°C for ten hours and all of the metal parts thoroughly outgassed in place by means of a high-frequency induction furnace. The vacuum attained after this procedure was of the order of 2×10^{-8} mm. The extent to which the tube had been outgassed was indicated by the amount of gas liberated when the tungsten surface was heated. If the temperature of the surface was raised to 2800°K there was no measurable increase in the pressure of the residual gas provided the walls were kept cool. If they became hot, however, the pressure rose to over 10^{-5} mm. This gas was re-adsorbed by the walls and metal parts of the tube upon cooling as evidenced by the fact that the pressure would diminish to its previous low value even though this test was carried on with the experimental tube shut off from the mercury diffusion pump by the magnetically operated cut-off.

[8] L. A. Dubridge, Phys. Rev. 37, 392 (1931).

Experimental

The response of the tungsten surface to mercury metastable atoms was determined during various stages of outgassing and the variations in this response as a result of heat treatment were carefully followed. Before discussing the variations attention must be called to two corrections which are necessary to make the various results comparable. The response of a surface depends not only upon its sensitivity but also upon the number of metastable atoms which reach it. This number depended upon the total number of mercury atoms present and upon the number of electrons emitted by the filament. Tests showed that the response of a given surface was proportional to the total number of mercury atoms present and also to the electron current from the hot cathode to the accelerating grid. In all of the following discussions all measures of comparative sensitivity have been corrected for variations in electron emission and in vapor pressure and are therefore referred to an equal number of impinging metastable atoms.

After the thorough outgassing described above the tungsten surface which had previous to outgassing been relatively insensitive to mercury metastable atoms was found to have increased in sensitivity from twenty to thirty times. Subsequent heating of the surface always resulted in marked temporary changes following which, however, the sensitivity soon returned to a value which varied on the average not more than ten percent over a period of several months, during which time the surface was subjected to numerous and varied heat treatments. This indicated that rather constant conditions had been obtained, in particular that of residual gas pressure. Under these favorable conditions, heating of the surface caused very significant changes in its response to mercury metastable atoms, which were investigated in detail by numerous tests extending over a period of many months.

The most interesting changes in the sensitivity of the surface were those following the heating of the surface to temperatures sufficiently high t_0

clean the tungsten surface of all surface films, that is between 1800°K and 2900°K.[9] The changes are shown in Fig. 2, which is typical of those obtained under the conditions described above. The electron currents from the surface due to the action of the metastable atoms upon it are plotted in arbitrary units as ordinates against time in minutes as abscissas.

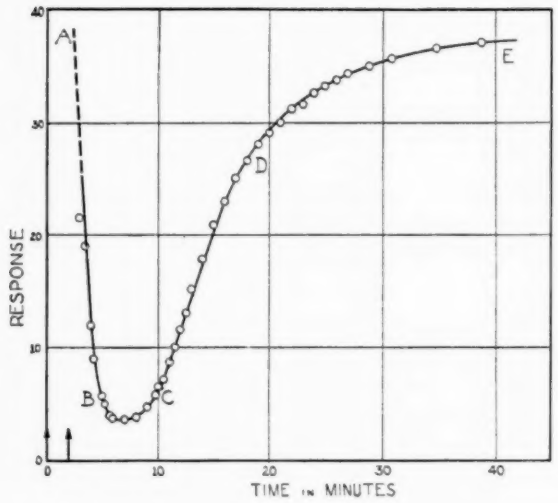

FIG. 2. Curve showing the change of response of tungsten surface with time, following cleaning by heating to 2250°K for 2 minutes. Tube temperature maintained at −5°C. Arrows show time when heating current was turned on and off.

On this curve and on succeeding curves the times at which the heating current was turned on and off are indicated by arrows. During the first three or four minutes after the surface had been cleaned by heating the sensitivity dropped sharply; portion *AB* of the curve. This drop was followed by a broad minimum, *BC*, which was followed after a few minutes by a fairly constant rise in sensitivity lasting many minutes, *CD*. The sensitivity finally reached a value, *E*, which was nearly the same in all of the repeated tests. This constant value will be referred to as the normal response of the surface. The same type of curve was obtained whenever the surface was heated to a temperature above 1800°K, whether the period of heating was a few seconds or as long as an hour.

[9] I. Langmuir and K. H. Kingdon, Phys. Rev. **34**, 129 (1929); I. Langmuir, Ind. and Eng. Chem. **22**, 390 (1930); I. Langmuir and Villars, J. A. C. S. **53**, 486 (1931); K. B. Blodgett and I. Langmuir, Phys. Rev. **40**, 78 (1932).

Furthermore, curves of the same general shape were obtained for a wide range of mercury vapor pressures. The constancy and reproducibility of this effect is indicated by the fact that fifty such tests scattered over a period of several months gave practically the same results.

The initial drop *AB* varied as to rate in the different tests made but was always too rapid to permit detailed study; consequently the conditions affecting it were not well established nor was there any clearly established evidence as to the cause of the sensitivity during this period. However, from the rate at which this drop takes place, it seems probable that immediately following the cleaning at high temperatures, the surface had relatively to the normal, a high value of sensitivity which dropped quickly to a value very much lower than this normal value.

The period *BC*, following this rapid drop in sensitivity and preceding the period of more rapid increase in the sensitivity varied considerably in duration in the different tests made. In the case illustrated in Fig. 2, the minimum value of the response during this period was ten percent of the normal value. In other tests the minimum response was only two or three percent. That this minimum value is not nearer to zero seems to be due to the overlapping of the initial process of decay of sensitivity and the process of recovery which is so marked in the stage *CD*, and to the amount of a few percent, to a feeble photoelectric effect from the radiation excited in the tube. Some of the response at this stage may also be due to the failure of the ends of the surface to receive the same heat treatment as the rest because of the cooling effect of the leads.

In the earlier part of the period *CD*, following this period of low sensitivity, the recovery of sensitivity was at an approximately constant rate. This together with the fact that this steady rise continued as a rule over a period of the order of ten minutes, permitted this portion of the curve to be studied in detail and more completely than was possible with the other portions.

RÔLE OF MERCURY IN SENSITIZATION

The well-known variations in photoelectric response with the gas content of a surface suggested that the change in response to metastable atoms described above were due to the presence

of residual gas or mercury vapor. It must be remembered in this connection that in these experiments the concentration of mercury atoms was always very much greater than that of the residual gas atoms. The residual gas pressures were of the order of 10^{-8} mm while the mercury vapor pressure was of the order of 10^{-4} mm. The part played by mercury vapor in the recovery of sensitivity of the surface was determined by varying the concentration of mercury atoms while maintaining the residual gas pressure as low as possible. While in general curves similar to that shown in Fig. 2 were obtained for various mercury vapor pressures, the slope of the rising portion of the curve, *CD*, was found to change with the vapor pressure. This indicated that the sensitive surface forming during this period was the result of a deposit of mercury atoms. That this increase in sensitivity during the period *CD* was due to such a deposit of mercury atoms was carefully checked in four ways.

(1) Observations were made of the effect of different concentrations of mercury atoms on the rate of recovery of the sensitivity of the surface as indicated by the slope of the rising portion *CD* of the curve.

(2) Observations were made of the effect of heating the surface at various stages during the recovery *CD* to temperatures at which one might expect mercury deposits to be driven off.

(3) Observations were made of the effect of removing the mercury vapor at various stages of the recovery process. This was done by immersing the lower half of the tube in a mixture of solid CO_2 and alcohol, temperature -78°C, at which temperature the mercury vapor pressure is only 3×10^{-9} mm.[10]

(4) After heating the surface at temperatures sufficiently high to clean it, observations were made of the effect of maintaining the surface at temperatures which would prevent the deposit of mercury atoms.

The tests are described below in detail:

(1) After heating the surface to some temperature between 1800°K and 2800°K in order to clean it, the changes in its sensitivity were followed for a few minutes beyond stages *AB* and *BC* until the rate of increase of sensitivity was practically constant. This rate was determined, and then the vapor pressure was quickly changed by the substitution of another constant temperature bath around the tube, and the new rate of increase determined. The results of such a test are shown in Fig. 3. The surface was first heated

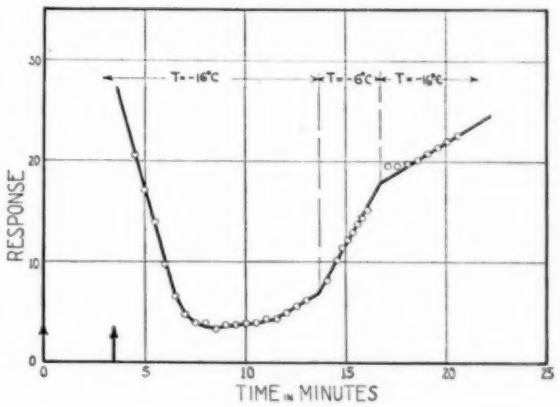

FIG. 3. Curve showing the effect of change of mercury vapor pressure upon the response curve. Surface cleaned at 2250°K for 3 minutes. Temperature of tube maintained at -16°C from $t=0$ to $t=13$ minutes, at -6°C from $t=13$ to $t=17$ minutes and at -16°C from $t=17$ minutes to $t=21$ minutes.

at 2250°K for three minutes with the temperature of the tube at -16°C. After the sensitivity had passed through the minimum, *BC*, and had begun to recover at a steady rate as indicated by the constant slope of the curve, the temperature of the tube was suddenly raised ($t=13$ minutes) to -6°C. The rate of change of sensitivity was again nearly constant but larger than before. At $t=17$ minutes when the temperature was restored to -16°C the rate of change of sensitivity returned to its earlier value. The ratio of the slopes of the curves at the two temperatures, -6°C and -16°C, is 3.0 and the ratio of the concentrations of mercury atoms present at these temperatures is 3.1. The rate of recovery of the surface was therefore proportional to the number of mercury atoms present. This test was repeated for many different changes of vapor pressure, and in all cases within the precision of the measurements the rate of recovery was found to be proportional to the number of mercury atoms present. In Fig. 3, the two points at $t=17$ and 17.5 minutes do not lie on the straight line because of a lag in the thermal equilibrium following the

[10] F. E. Poindexter, Phys. Rev. **26**, 859 (1925).

change in bath temperatures. In reducing the response to that for equal numbers of metastable atoms it was assumed that the temperature of the experimental tube changed immediately with the change of bath temperature. This lag was determined directly by using the tube as an ionization manometer to measure the varying mercury vapor pressure, and so long as the quantity of mercury was restricted to a few small drops it was of the order of one minute.

(2) A series of tests were made in which the surface was heated to temperatures between 800°K and 1400°K for a short interval during the recovery process, so as to drive off any mercury which might have deposited upon it. Fig. 4 shows

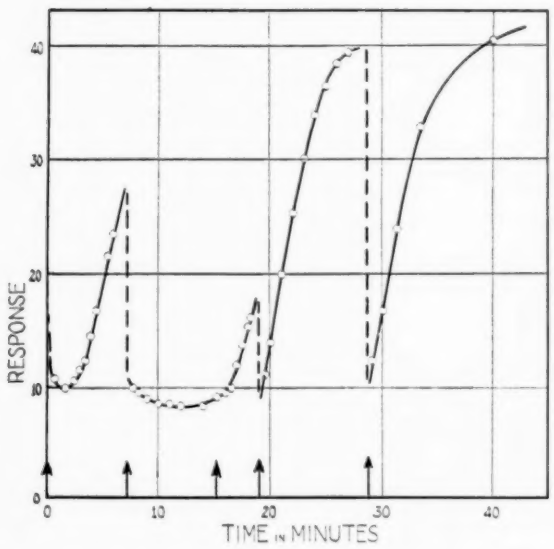

FIG. 4. Curve showing the effect of heating the surface to temperatures of 1320°K and 800°K. Surface cleaned at $t=0$ by heating to 2420°K for 10 seconds. From $t=7$ to $t=14.5$ minutes surface maintained at 800°K. At $t=19$ and at $t=28.5$ minutes, surface was heated to 1320° for 10 seconds.

a typical result. In this test the surface was first cleaned by heating at 2420°K for ten seconds, after which the usual changes in sensitivity were observed, the response dropping sharply at first, passing through a minimum, and then rising at a fairly steady rate. After this rise had proceeded for a few minutes, the temperature of the surface was raised, at $t=7$ minutes, to 800°K whereupon the sensitivity dropped and remained low as long as this temperature was maintained. The current which heated the surface was then cut off at $t=14.5$ minutes and the sensitivity was observed to rise again at a fairly constant rate. At $t=19$ minutes the surface temperature was raised to 1320°K for ten seconds and immediately thereafter the sensitivity was found to be very low, but rose again at a nearly steady rate. Repetition of this heat treatment at $t=28.5$ minutes gave the same result, an immediate loss of sensitivity followed by a steady recovery.

Fig. 5 shows another example of this phenomenon. The first three sections of the curve, (a), (b), (c), show the effect on the sensitivity of heating the surface to 1320°K for ten seconds with the mercury vapor pressure held at 2×10^{-4} mm (0°C) throughout the test. The surface had been previously cleaned at high temperature and had been allowed to recover to its normal value and was then heated to 1320°K for ten second intervals at times $t=0$, 6 and 18 minutes. The sensitivity was in each case reduced to approximately ten percent of the normal value by the heating but thereafter the sensitivity recovered at practically the same rate in each case. The sections marked (c) and (d) show repetitions of the same heat treatment, but at mercury vapor pressures of 8×10^{-5} mm and 6×10^{-5} mm, respectively, corresponding to temperatures of -8°C and -10°C. Tests of this kind were repeated many times and always showed as a result of heating the surface to temperatures in the neighborhood of 1300°K, this same sharp drop in sensitivity, which seems to be best explained as due to evaporation of a layer of mercury atoms from the surface.

Immediately after such heating the response of the surface was always a small fraction of its previous value, in Fig. 5 about one-tenth, in other cases even less. As already pointed out the failure of the ends of the surface to receive the same heat treatment as the rest of the surface, due to the cooling effect of the leads, probably accounts for the fact that the sensitivity to metastable atoms is not reduced to zero by the heating.

The rate at which the recovery took place was found in these tests, as in (1), to be approximately proportional to the mercury vapor pressure. In Fig. 5, the ratios of the slopes of the -8°C curve and the -10°C curve to the slope of the 0°C curve are 2.1 and 2.8, respectively, while the corresponding ratios of the number of mercury atoms

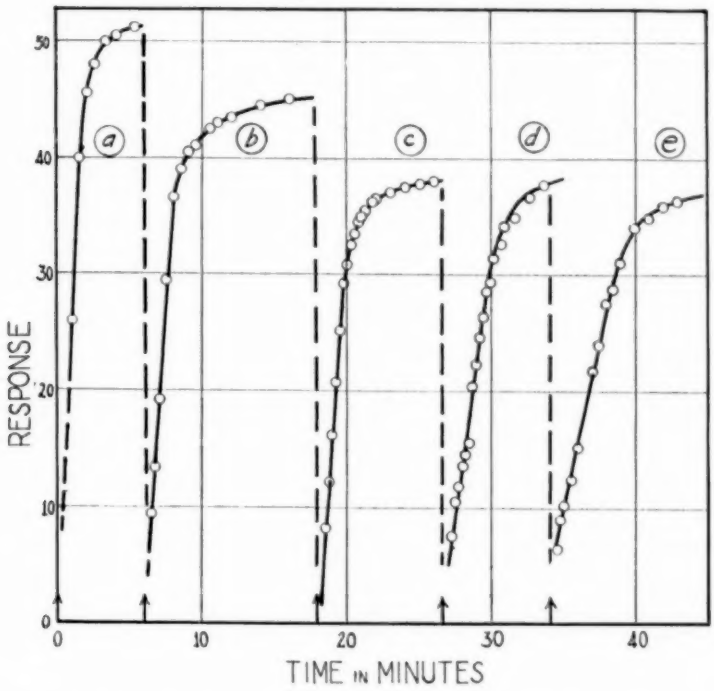

FIG. 5. Curve showing effect of heating surface to 1320°K for 10 seconds, at $t=0$, 6, 18, 26.5 and 33 minutes. Curves (a), (b) and (c) tube temperature maintained at 0°C, curves (d) and (e) tube temperature maintained at -8°C and at -10°C, respectively.

present at these temperatures to the number present at 0°C are 2.4 and 2.9, respectively.

(3) The purpose of this test was to determine the effect upon the changes in response of the surface of reducing the concentration of mercury atoms to a very small amount. This was done by immersing the lower half of the tube in a mixture of solid CO_2 and alcohol, temperature -78°C which reduced the mercury vapor pressure to 3×10^{-9} mm, approximately 0.00001 of the pressure at 0°C. The effects of such treatment is shown in Fig. 6, (a), (b), (c), (d). The surface was cleaned by heating at 2420°K and after it had almost completely recovered its normal sensitivity (curve (a)), the surface was heated at $t=14$ minutes to 1320°K for ten seconds. The sensitivity which was thus reduced to a low value recovered in the usual manner, curve (b). To compare with this we have curves (c) and (d). In these two tests the procedure was the same as for (b) except that before the surface was heated to 1320°K the mercury vapor pressure was reduced to 3×10^{-9} mm (-78°C). This value of the vapor pressure was maintained following the heating for periods of two and ten minutes in these two tests respectively, after which the vapor pressure was brought back to 2×10^{-4} mm (0°C). In each case the sensitivity then recovered in the usual manner starting from a value close to zero. We see then that in the absence of mercury atoms no appreciable recovery of sensitivity took place following the 1300°K heating, but that as soon as the mercury atoms were again present, the recovery of the surface started.

That the process of recovery stopped or was greatly retarded by the removal of mercury atoms is indicated by other tests made under somewhat different conditions. A typical curve is shown in Fig. 7. The surface was heated to 2420°K for 30 seconds and after the response had passed through the first two or three stages and the sensitivity was steadily rising, the mercury vapor pressure was reduced to 3×10^{-9} mm (-78°C). This was maintained for fifteen minutes (from $t=3.5$ to $t=18.5$ minutes) and then the pressure was raised to 2×10^{-4} mm (0°C). Although there was considerable uncertainty in the extrapolation of the curve between $t=18.5$ and

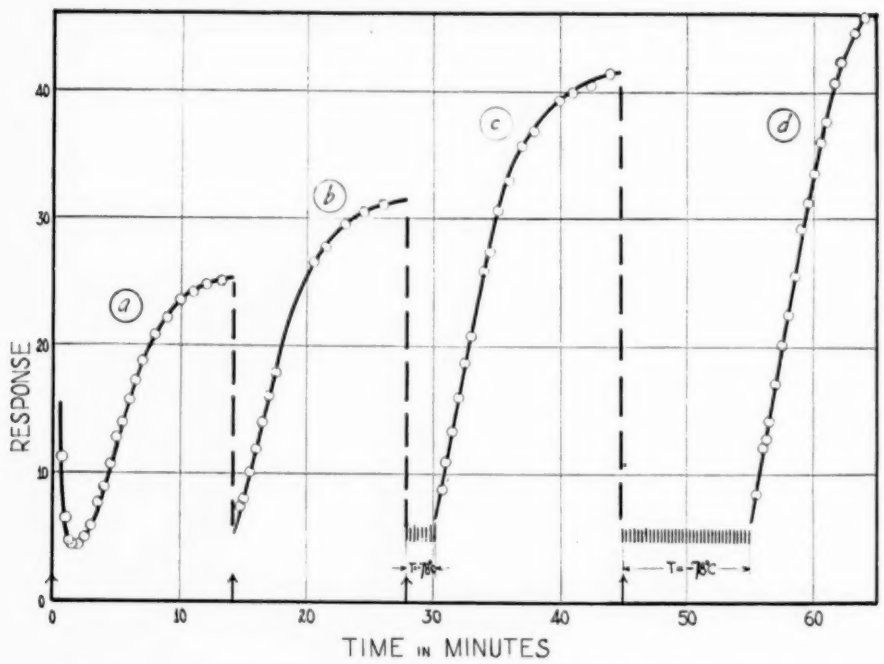

FIG. 6. Curve showing the effect of maintaining the temperature of the tube at −78°C for an interval following heating the surface to 1320°K. Surface cleaned at $t=0$ by heating to 2420°K for 10 seconds. Surface heated to 1320°K for 10 seconds at $t=14$, tube temperature 0°C. At $t=28$, surface heated to 1320° for 10 seconds, tube temperature maintained at −78°C for 2 minutes, then restored to 0°C. At $t=44$, surface heated to 1320°K for ten seconds, tube temperature maintained at −78°C for 10 minutes, then restored to 0°C.

$t=19$ minutes, made necessary by the lag in the temperature equilibrium, if we assume that the slope of the curve after the interruption was equal to or even greater than before it is seen that little or no recovery of the sensitivity took place. Tests to be described later showed that this assumption was justified.

Similar delay in the recovery process was observed when the surface was cleaned by heating to temperatures above 1800°K in the absence of mercury vapor. In such tests the recovery process was delayed many minutes until the mercury vapor pressure was restored. The curves obtained were similar to the recovery curve shown in Fig. 2, except that the initial drop AB was not observed and the rest of the curve was displaced in time by the interval during which the mercury atoms were kept from the surface by the low temperature bath.

It should be remembered that in these tests only observations taken during the first minute after replacing a −78°C bath with a 0°C bath are somewhat in error because of a lag in the establishment of a thermal equilibrium. This thermal lag is shown in curve (b) of Fig. 8, which shows the change as measured by ionization currents, in the concentration of mercury atoms following this change in the bath temperature.

(4) This test consisted in heating the surface to high temperatures to clean it of all gas films or oxides after which the temperature was reduced to about 1300°K. This latter temperature was maintained for several minutes and the surface then allowed to cool. The subsequent response showed that while the surface was kept at 1300° K the recovery process was delayed. The recovery of the surface then proceeded in a manner similar to the typical recovery curve shown in Fig. 2. The dropping portion, AB, however, was not observed and the rest of the curve was shifted in time by the interval during which the surface was maintained at 1300°K. This delay in the recovery process indicates that at these temperatures the mercury atoms either fail to condense upon the surface at all, or else do not remain in sufficiently large quantities to form

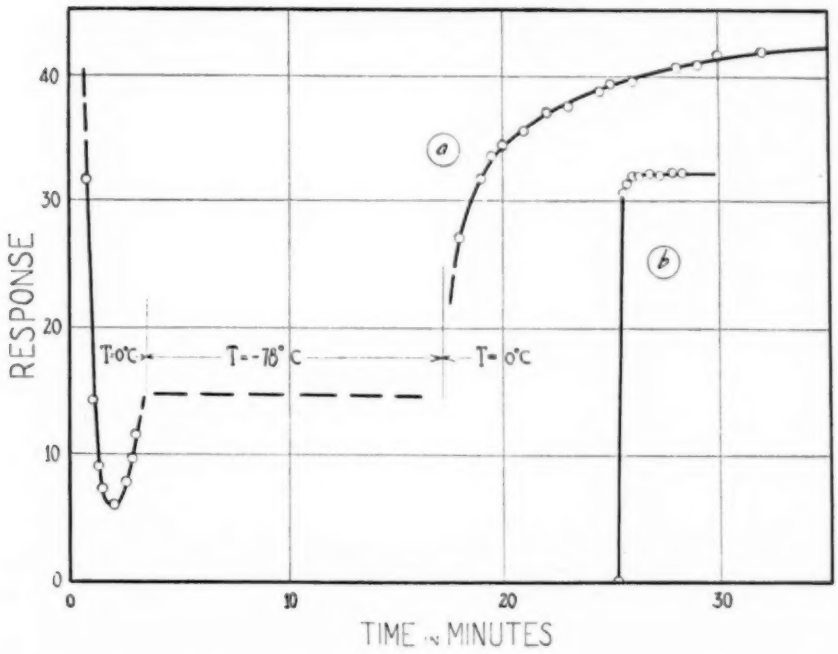

FIG. 7. Curve (a) shows the effect of reducing the tube temperature to −78°C at $t=3.5$ minutes, and maintaining this temperature to $t=18.5$ minutes. Tube temperature maintained at 0°C from $t=0$ to $t=3.5$, and from $t=18.5$ to $t=32$. Surface cleaned by heating at $t=0$ to 2420°K for 30 seconds. Curve (b), ionization currents, showing rate at which mercury vapor pressure reaches equilibrium, when the tube temperature is changed from −78°C to 0°C.

nuclei from which the growth of a surface could proceed. This is in accord with results of other observers. Wood[11] has reported the failure of atoms to condense upon a surface above a critical temperature. Again, Estermann[12] found in experiments with molecular beams of mercury and cadmium that a very narrow beam failed to produce a deposit upon a target, while a wider beam in which the concentration of the atoms was no larger did produce a deposit. This indicates that it was necessary to have some minimum number of atoms condensed upon a surface to form a nucleus for the growth of an extended surface.

The tests just described showed that the sensitivity of the metal surface, after each temporary change in sensitivity due to heat treatment returned in time to the normal value, which because of its constancy points strongly to a definite equilibrium structure of the surface. These tests further brought out that the formation of the surface involves mercury atoms as shown by the observations that the rate of recovery varied directly with the concentration of mercury atoms surrounding the surface, that the removal of

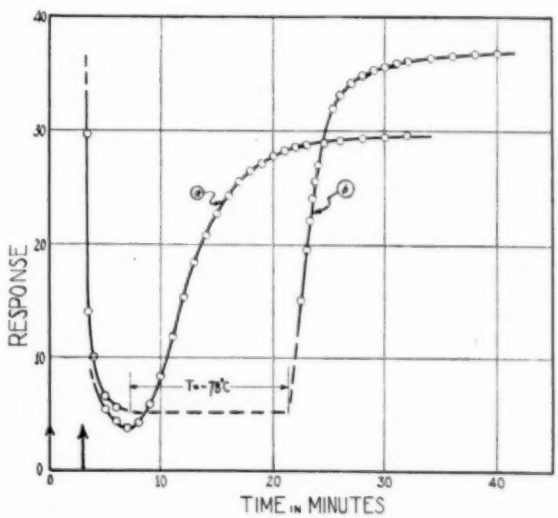

FIG. 8. Curve (a) shows the usual recovery curve, after heating the surface to 2100°K for three minutes, tube temperature 0°C throughout the test. Curve (b) shows the effect of reducing the tube temperature from $t=7$ to $t=21.5$ minutes to −78°C.

[11] R. W. Wood, Phil. Mag. **32**, 364 (1916).
[12] J. Estermann, Zeits. f. Physik **33**, 320 (1925).

mercury vapor from the tube or the prevention of a deposit of mercury on the surface by suitable heating stopped the process of recovery of sensitivity, and that heating a surface during the recovery process to a temperature presumably sufficient to drive off mercury deposits again reduced the sensitivity to a very low value. In the next section further evidence as to the nature of the sensitive surface will be discussed.

It is of interest to note that the changes observed in the sensitivity of the surface were not due to the action of the metastable atoms themselves. The same changes in sensitivity were observed whether or not the source of potential exciting the metastable atoms was cut off between readings.

Rôle of Oxygen in Sensitization

Returning again to the typical curve shown in Fig. 2 we note that between the period of quick decay of sensitivity AB, which follows the heating of the tungsten surface to a temperature sufficient to clean it of all oxide or oxygen layers, and the period of steady recovery of sensitivity CD, several minutes elapse during which time some relatively slow change takes place in the surface which appears to prepare it for the reception of mercury atoms.

The following tests seem to throw light on the nature of this change. In Fig. 8 (a) is shown the normal behavior of the surface after cleaning by heating to 2100°K for three minutes, the vapor pressure being 2×10^{-4} mm (0°C). In Fig. 8 (b) the surface was treated under the same conditions except that between $t=7$ and $t=21.5$ minutes the mercury vapor pressure was reduced to 3×10^{-9} mm (−78°C). As soon as the vapor pressure was restored to 2×10^{-4} mm (−0°C) the sensitivity started to rise, as in previous tests. However, it will be noted that the rate of rise in (b) is several times greater than in (a). In addition to the more rapid rise in sensitivity it will be noted that the response of the surface in test (b) rose to a value approximately 20 percent higher than in test (a). It is seen then that not only is the recovery of the surface delayed in the absence of mercury atoms as already noted, but that when the mercury atoms are brought back after such an interval more rapid formation of the sensitive surface follows and the sensitivity reached is somewhat greater. Subsequently the sensitivity dropped slowly back to the normal value.

Fig. 9 shows the result of keeping the mercury atoms from the surface for an extended interval by maintaining the surface at 800°K. For purposes of comparison, curve (a) shows the usual changes in sensitivity following cleaning of the surface by heating. In the test shown by curve (b) the surface was similarly cleaned by heating at 2250°K but the heating current was then reduced for about twenty minutes to a value which maintained the surface at a temperature of 800°K, after which the surface was allowed to cool. The sensitivity in this case also dropped sharply but instead of rising as in (a) the sensitivity increased but little until the surface was allowed to cool, at $t=32$ minutes, when the sensitivity rose very rapidly, at a rate several times greater than in (a), indicating that during the period when the deposit of mercury atoms was to some extent prevented, some changes were taking place which rendered the surface more susceptible to the subsequent deposit of a sensitive layer of mercury atoms.

Both of these results show that if a clean surface is kept free from deposits of mercury for some time a change takes place on the surface which accelerates the formation of the sensitive

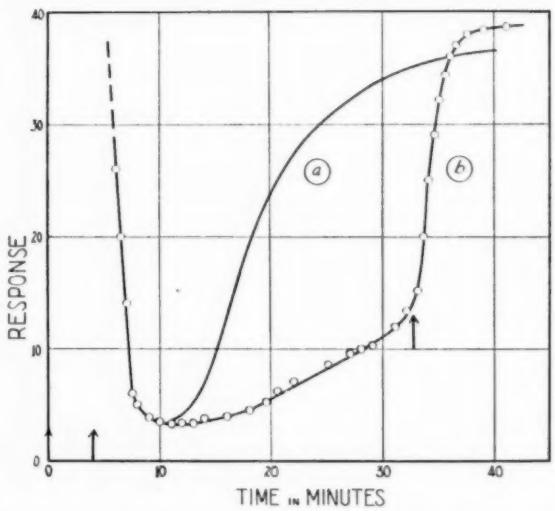

Fig. 9. Curve (b) shows the effect of maintaining the surface temperature at 800°K from $t=4$ to $t=32$ minutes following cleaning of the surface by heating to 2250°K from $t=0$ to $t=4$ minutes. Surface temperature reduced to tube temperature, at $t=32$ minutes. Curve (a) typical response curve with surface at tube temperature throughout the test.

deposit of mercury and also permits the building up of a more sensitive layer. This characteristic, as well as other results to be discussed later, indicates that the surface responding to mercury metastable atoms does not consist simply of a mercury film on the tungsten but is a more complicated surface involving gas atoms, presumably oxygen atoms. Such complex surfaces have been found in thermionic and photoelectric work to give responses which show similar variations as a result of the heat treatment. For example, surfaces consisting of barium films on platinum or of thorium films on tungsten show changes with heat treatment, which indicate that the response is determined by the fraction of the surface that is covered by such films. The changes in response following heat treatment of a surface on which there are in addition to such a metal film some gas atoms (as for example, surfaces such as Th−O−W, Cs−O−W, Ba−O−Pt and Cs−O−Ag) are found to be much more varied and complicated and dependent not only upon the fraction of the surface which is covered by the deposited metal and oxygen atoms, but also upon the order of their deposition.[13] Becker[14] has advanced the hypothesis that these layers of oxygen and barium in the case of oxide coated platinum filaments diffuse and reform as a result of thermal agitation, and that the sensitivity depends not only upon their relative amounts but also upon their relative positions. In these present experiments, the variations of the response of the tungsten surface to metastable atoms as a result of heat treatment indicate a complex surface of similar nature. It is well known that layers of oxygen form on tungsten[9] and it may be noted that the time elapsing between the cleaning of a surface at high temperatures and the beginning of its subsequent recovery, three or four minutes, is approximately the time required for the formation of such an oxygen layer. Dushman[15] has calculated from kinetic theory that at a pressure of 2×10^{-6} mm a monomolecular layer of oxygen forms on a thorium film on a tungsten surface in one second assuming as deduced by Langmuir that every atom that strikes the surface sticks to it. In the present experiments the residual gas pressure was of the order of 10^{-8} mm at which pressures the formation of such a layer would from this result require several minutes, which is the interval observed above.

In the light of the above discussion, the various stages of the curve shown in Fig. 2 may be explained as follows: Since heating the surface to 2500°K is sufficient to drive off completely any oxygen layers or oxides which form on the tungsten, we may assume that after such heat treatment the surface of the tungsten was clean, On this surface we could expect a deposit of mercury atoms and oxygen atoms, but at the concentrations obtained in these experiments a deposit of mercury atoms could have been almost instantaneous, whereas several minutes would have been required for any extended oxygen layer to form. Now, the response to metastable atoms observed immediately after cleaning of the tungsten was high but fell rapidly (see *AB*, Fig. 2). Since this response was observed within a fraction of a minute after the cleaning, the surface must have been either pure tungsten, or tungsten covered with a layer of mercury atoms. The decrease of sensitivity thereafter seems best explained as due to a deposit of oxygen upon the pure tungsten by either a displacement of the mercury layer by the oxygen layer or by a deposit of oxygen upon the mercury. We may conclude that any such surface covered with oxygen atoms would be insensitive from the fact that a large work function is found for it in thermionic and photoelectric experiments. In tests to be described later oxidized surfaces were actually found to be very insensitive to mercury metastable atoms.

That the initial decrease in sensitivity as shown by the part of the curve (*AB*) was occasioned by oxygen is also indicated by the behavior of the surface in a test previously described. In this test the surface was cleaned by heating to 2500°K in the absence of mercury vapor, (−78°C). After the lapse of several minutes the vapor pressure was raised to 2×10^{-4} mm (0°C) and the subsequent variations of sensitivity consisted only of the stages *BC* and *CD*, while the stage *AB* was not observed. Since only residual gas, presumably oxygen, was present during the

[13] Hughes and Dubridge *Photoelectric Phenomena*, pp. 171 ff.; S. Dushman, Rev. Mod. Phys. **2**, 440 (1930).

[14] J. A. Becker, Phys. Rev. **34**, 1345 (1929).

[15] S. Dushman, Rev. Mod. Phys. **2**, 447 (1930).

interval in question the failure to observe the high initial sensitivity and subsequent rapid decay may be attributed to the action of such gas atoms on the surface.

During the stage *BC*, the surface remained relatively insensitive for several minutes. During the interval, mercury atoms which reached the surface either failed to deposit upon it or the surface which they form by condensing on the oxygen layer was one which was not sensitive to mercury metastable atoms. Some further change must have taken place before the sensitive layer of mercury atoms was formed. Possibly there was some rearrangement of the oxygen and mercury atoms already on the surface during which the oxygen diffused down to the pure tungsten resulting in an oxygen on tungsten surface upon which mercury atoms deposited and formed a sensitive surface during the stage *CD*. In the stage *DE* the sensitivity gradually approached a constant value when apparently there was some kind of equilibrium established so far as the effective part of the surface was concerned. As has been pointed out this equilibrium or normal value remained very nearly constant as the surface stood and was practically the same after each heat treatment no matter how extensive. However, there is evidence that the lower layers, of this surface, which seemed to consist of a number of atomic layers, continued to change for many hours after the sensitivity had ceased to change measurably. It was found that a surface which had been left without heat treatment for several hours behaved upon being heated for a few seconds to a temperature in the neighborhood of 1300°K quite differently from a newly formed surface. As has been seen (see Fig. 7) with the latter such treatment always resulted in an almost complete loss of sensitivity. With the aged surface, on the other hand, the result was quite different. This is shown in Fig. 10, (a), (b) and (c). The surface which had been standing for many hours was heated to 1300°K for ten seconds. Instead of falling to a low value as with a newly formed surface, the sensitivity immediately after the heating was found to be five or six times greater than that of the normal surface. This sensitivity fell rapidly at first, then more slowly and gradually returned to the value observed before this heating. This was repeated (curve b) with like result and in general could be repeated three or four times in succession, but after several repetitions or if the temperature of the surface was maintained at 1300°K for a prolonged interval, this effect disappeared and reappeared only after the surface had been left again for many hours without heat treatment. This behavior seems to show that as the surface aged the atoms in the lower layers tend to diffuse and form a thin layer of mercury, possibly monatomic on a similar layer of oxygen. When this surface is heated to 1300°K for ten seconds only the outer layers of mercury and oxygen are evaporated while the thin layer of mercury is bound too tightly to the oxygen to be easily driven off, as in the case of the newly formed surface. The higher value of the sensitivity resulting from the heating seems to bear out the assumption that the normal surface has a substructure which has a more efficient disposition of the atoms forming it. The subsequent decay of sensitivity back to the normal value indicates the formation of complex layers of mercury and oxygen atoms as further deposits of oxygen take place. The prolonged or repeated heating apparently destroys the formation of this substructure either by displacing the atoms by thermal agitation or by evaporation.

To determine whether or not the decay of the sensitivity in the above test was caused or influenced by mercury atoms, this experiment was repeated with various values of mercury vapor pressures. Further the concentration of the mercury atoms was varied during the period when the sensitivity was falling by changing the mercury vapor pressure rapidly from one value to another. Neither of these tests showed any influence of the mercury vapor pressure upon the rate at which this decay of sensitivity took place. Again a repetition of the test in the absence of mercury atoms that is with the tube in a bath of temperature -78°C showed that this decay still occurred and at the same rate. Removing the mercury atoms during the progress of this decay by cooling to -78°C similarly had no effect upon this phenomenon. This last result is shown in Fig. 10 (c) which shows the effect of reducing the vapor pressure to a very small value between $t=27$ and $t=33$ minutes. Disregarding the first three points following $t=33$ minutes, which are low because of the lag in the vapor pressure, we

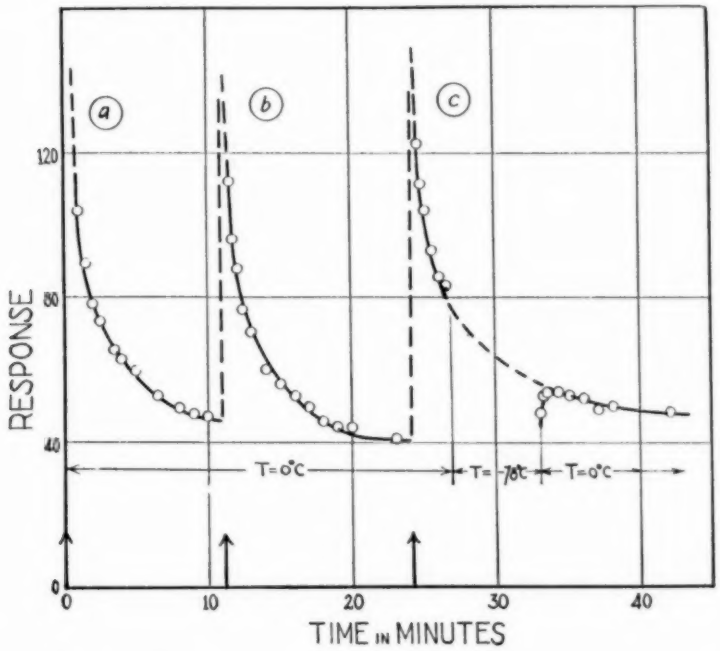

FIG. 10. Curves showing the effect of heating an aged surface to 1300°K for 10 seconds, at times $t=0$, 11 and 24 minutes. Curves (a), and (b) tube temperature=0°C throughout, curve (c) temperature changed to −78°C from $t=27$ to $t=33$ minutes.

see, comparing the curve with 10 (a), that the falling off of sensitivity was not affected during this six minute period. It seems therefore, that this loss of sensitivity depends either upon the action of the residual gas or upon a rearrangement of the atoms on the surface by some diffusion process.

In order to study more directly the part played by oxygen in the formation of the sensitive surface, the effect of increasing the concentration of oxygen in the tube was investigated. The pumping system was filled to a pressure of one or two centimeters with oxygen from which all condensible vapors had been removed by passing the oxygen through a drier and a long narrow helix of glass submerged in liquid air. The system was then pumped out and this process repeated many times to flush out the system. Finally oxygen at a pressure of 0.02 mm was allowed to enter the experimental tube and the tungsten surface heated in this atmosphere for a few seconds at 1200°K for the formation of an oxygen layer on the tungsten, as described by Langmuir and Kingdon.[16] Following this, the surface was found to be very insensitive to the action of mercury metastable atoms, the response being approximately one-thousandth of the response of the equilibrium surface described above. This was in agreement with previous work in which oxidized surfaces were found to be quite insensitive although in the present case no oxide was visible.

The tube was then systematically outgassed and the response to metastable atoms observed as the gas content of the tube and the metal parts was reduced. The variations in sensitivity of the surface following heat treatment were also watched during this time. After repeated baking of the tube and repeated outgassing of all of the metal parts by means of the high-frequency furnace the sensitivity of the surface returned to the value it had previous to the admission of oxygen to the tube. In the final stages of the outgassing not only was the same sensitivity obtained, but the same variations in sensitivity

[16] I. Langmuir and K. H. Kingdon, Phys. Rev. **24**, 510 (1924).

following the heating of the surfaces were also observed. However, at two stages of the outgassing there were observed differences in this behavior which seemed very significant.

During the earlier stages the oxygen content of the metal surfaces was large as indicated by ionization manometer measurements taken when the tungsten surface was heated, the tube being shut off from the pumps by the magnetically operated cut-off. Pressures of the order of 10^{-5} and 10^{-6} mm were observed, but this gas was immediately readsorbed by the metal surfaces when they cooled. At this stage of the outgassing process the changes in sensitivity following the heating of the tungsten surface to clean it were significant in that immediately following heating the sensitivity instead of being high as usually observed was very low. The surface thereafter recovered its sensitivity in the usual manner, the recovery curves being similar to the typical curve shown in Fig. 2, except for the fact that the stage AB was not observed. This indicated that with relatively large amounts of oxygen present this drop in sensitivity either took place too rapidly to be observed or that the high concentration of oxygen atoms prevented the formation of a sensitive surface immediately following the cleaning.

As the outgassing proceeded another stage was reached in which the oxygen content was such that the changes in sensitivity to metastable atoms following cleaning of the surface were markedly different. The sensitivity immediately following heating of the surface was found to be very much increased, in some instances by a factor of more than fifty. This high sensitivity was very short lived and dropped very rapidly back to the value observed before the heating but did not fall below this value at any time. The rapid rate at which the sensitivity dropped in these cases, indicated that the initial sensitivity may have been even greater than recorded. From the high sensitivity obtained in photoelectric and thermionic phenomena with surfaces consisting of thin metal films on similar films of oxygen, as for example, CsO—Ag, and Cs—O—W surfaces, it seems likely that the high sensitivity observed under these conditions resulted from an analogous surface probably composed of a thin layer of mercury on a similar oxygen layer on the tungsten. The subsequent drop of sensitivity may then have been due to the deposit of more oxygen and mercury atoms forming a thicker and less sensitive surface, which, however, was very stable. This behavior of the surface following heating was observed for only a very brief period. Apparently it depended upon having the oxygen at a certain critical pressure immediately after the cleaning at high temperatures. With larger pressures too rapid deposition of the oxygen resulted, with smaller pressures the deposition was complicated by the relatively larger concentration of mercury atoms, so that this very sensitive surface could not be formed.

The marked changes in the sensitivity of the surface after oxygen had been admitted to the tube and throughout the series of tests made as the oxygen content was again gradually reduced confirm the hypothesis that oxygen is the gas which plays a fundamental rôle in the formation of the surface which responds to mercury metastable atoms.

The very high sensitivities observed during these latter tests permit an estimate to be made of the efficiency of metastable atoms in producing the emission of electrons from a metal surface. The fact that responses of some fifty to one hundred times the normal value were observed shows that with the normal surface not more than one or two metastable atoms out of a hundred were effective in causing the emission of an electron from the normal surface. This is of course an upper limit to the efficiency and is in agreement with the similar value of one in two hundred which Pike[17] has calculated for neon metastable atoms impacting upon outgassed iron. On the basis of these figures and the observed electron currents, the number of metastable atoms striking the surface per square centimeter per second in these experiments is of the order of 10^{10}, which from kinetic theory indicates a concentration of metastable atoms of 5×10^{7}.

The behavior of the tungsten surface due to heat treatment described above bears a marked similarity to the behavior of the metal probes used in mercury vapor by Webb and Sinclair.[18] In these latter experiments the contact potentials of the probes were changed to a large degree by the heating resulting from the electron current

[17] E. W. Pike, Phys. Rev. **40**, 314 (1932).

[18] H. W. Webb and D. Sinclair, Phys. Rev. **37**, 186 (1931).

and upon cooling went through a series of changes lasting in some cases several minutes. The result was that the probe characteristics did not repeat when taken first with increasing voltage and then with decreasing voltage or *vice versa*. In general, the curves obtained depended largely upon previous treatment of the probes and the rate of taking observations. It was found also that the presence of traces of oxygen in the tube caused more rapid and violent variations in the contact potentials of the probes. It seems probable that these probes had layers of mercury and oxygen atoms deposited upon them similar to those on the surface described in the present paper.

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This investigation was undertaken at the suggestion and with the guidance and advice of Professor Harold W. Webb, to whom thanks and appreciation are herewith extended.

On the Constitution of Metallic Sodium

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Previous developments in the theory of metals may be divided clearly into two parts: that based principally upon the hypothesis of free electrons and dealing with conductivity properties, and that based upon calculations of valence forces and dealing with the chemical properties. In the present article an intermediate point of view is adopted and the free-electron picture is employed in an investigation of chemical properties of metallic sodium. The assumption is made that in the metal the K and L shells of an atom are not altered from their form in the free atom. The properties of the wave functions of the electrons are discussed qualitatively, first of all, and it is concluded that the binding energy will be positive even when the Pauli principle is taken account of. This is followed by a quantitative investigation of the energy to be associated with the lowest state. First of all it is shown to what extent the present picture takes account of the interactions of electrons with both parallel and antiparallel spins, and to what extent remaining effects may be neglected. Next a Schroedinger equation is solved in order to determine the lowest energy level for various values of the lattice constant. To this a correction is made to account for the Pauli principle and from the result the lattice constant, binding energy and compressibility are calculated with favorable results.

I.

THE investigations which have been carried out so far on the constitution of metals by quantum mechanics may be divided into two classes, the work on conductivity and related phenomena, carried out chiefly by Bloch, Peierls, Nordheim and Brillouin[1] are mainly based on the hypothesis of free electrons[2] and are concerned with the interaction between the electronic motion and the vibrations of the lattice, which is responsible for the electric resistance. The works of the other class[3] are mainly concerned with the chemical properties and crystal structure of the metals and are based on calculations of valence forces. They encounter great mathematical difficulties because the application of the usual methods to calculate valence forces becomes more and more difficult as the number of atoms increases.

The present work intends to take an intermediate point of view by applying the free electron picture but aiming at a calculation of chemical properties of metallic sodium such as lattice constant, heat of vaporization, compressibility, etc. The method of calculation is the same one as that proposed by Hund for molecules[4] and more recently applied by Lenz and Jensen[5] to ionic lattices, and by Lennard-Jones and H. J. Woods[6] to two dimensional metallic lattices. The electrons are assumed to move freely in a potential field and their interaction is supposed to be contained to a large extent in this field, much as in Hartree's method of the self-consistent field which is actually the field adopted in the calculations of Lenz (not in ours). The initial assumptions which one makes about the statistical connections of positions of different electrons are necessarily rather rough in this picture and should be improved afterwards.

II.

We assume first that the electrons in the K and L shells are not affected by the metallic bond and their wave functions the same as in the

[1] Cf. the comprehensive treatment by L. Brillouin, Die Quantenstatistik. Berlin, 1932.

[2] Cf. W. Pauli, Zeits. f. Physik **41**, 81 (1927); A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

[3] J. C. Slater, Phys. Rev. **35**, 509 (1930); E. A. Hylleraas, Zeits. f. Physik **63**, 771 (1930); and especially H. S. Taylor, H. Eyring, A. Sherman, J. Chem. Phys. **1**, 68 (1933).

[4] F. Hund, Zeits. f. Physik **40**, 742 (1927) and applications of this point of view to crystals, Zeits. f. Physik **74**, 1 (1932).

[5] W. Lenz, Zeits. f. Physik **77**, 713 (1932); H. Jensen, Zeits. f. Physik **77**, 722 (1932).

[6] J. E. Lennard-Jones and H. J. Woods, Proc. Roy. Soc. **A120**, 727 (1928).

free state. This is justified since the corresponding wave functions practically vanish in half the interatomic distance. For the valence electron, however, such an assumption is quite out of the way, since the maximum of the corresponding wave function is (quite necessarily, as we shall see) just about half way between two atoms. Contrary to the conditions which exist in the free state, however, the wave function must not drop to zero after the maximum but can continue periodically through the whole crystal. It will therefore be much smoother than the wave function of the free atom, and the kinetic energy of the corresponding state will consequently be much smaller than that of the electron in the free atom. The potential energy, on the other hand, will be negatively larger in the lattice than in the free state because outside of the above-mentioned maximum the wave will not be under the influence of the nucleus considered originally, but under that of the next nucleus of the lattice, which is nearer. The electron with the wave function just described will have a larger negative energy than that in the free atom and we consider this to be the essence of the metallic state.

Of course, the wave function which one obtains by continuing the atomic wave function periodically in the lattice is not the real wave function of the free electron in the lattice, but the energy of the latter will be even smaller than that of the former. We shall try to find an approximation to the real wave function by actually solving a differential equation.

It must be added that not all the free electrons can be in the state given above, because of the Pauli principle. This reduces the magnitude of the metallic bond, because the electrons must have an additional kinetic energy, which is known as the zero-point energy of a Fermi gas. One sees easily, however, that this additional energy is smaller than the reduction of the kinetic energy which was obtained by continuing the wave function periodically through the whole lattice, so that there certainly remains a positive amount for the metallic bond.

III.

First, we shall calculate the energy of the free electron in the lowest state. We shall do this by numerically solving a Schroedinger equation. It will not be necessary to solve it for the entire lattice, because it will have the same symmetry as the crystal and hence will merely repeat itself a great number of times. Because of this symmetry, the derivative of the wave function at every crystallographic symmetry plane will be zero perpendicular to this plane. This will be used as a boundary condition. The crystallographic symmetry planes which we shall use in this way bisect perpendicularly the lines connecting the second nearest atoms. If we draw lines connecting the nearest atoms and consider the planes bisecting these perpendicularly, we have every atom surrounded by a truncated octahedron (Fig. 1).

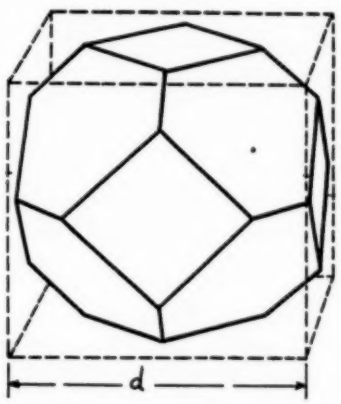

FIG. 1.

The middle points of the planes of the latter possess such symmetry (S_6) that the derivative of the wave function must vanish at these points in every direction. It will be quite a good approximation to replace the polyhedron of Fig. 1 by a sphere of equal volume, and to take as boundary conditions that the derivative of the wave function vanishes at the boundary of this sphere.

The determination of the potential function to be used inside this sphere is more difficult. It would be quite out of the way to use Hartree's method as the density of electrons in the greatest part of the domain is very small. This fundamental difference between metallic and ionic lattices was already pointed out by Lenz.[5] If we assume that two electrons are never around the same ion, every ion may be supposed to be surrounded by a spherical electron cloud which will

exactly[7] cancel its potential outside of the sphere. Hence it seems to be the best simple assumption to take the potential as that of the ion inside the sphere mentioned above. The knowledge of this potential will allow us to set down the differential equation for the free electron which will be solved with the boundary condition that the derivative vanish at the boundaries of a sphere. The solution will be obviously spherically symmetric about each atom, which is of course not true for the actual wave function of the free electron but is a consequence of our approximations. It is not very far from the truth, however, since the wave function will actually have the highest crystallographic symmetry (0^h) which is not very far from spherical symmetry, for to every direction there are not less than 47 other equivalent directions.

The justification of the assumption that two electrons are never around the same ion arises from two sources. Consider first the statistical connections between the positions of two electrons in an ideal Fermi gas. The complete wave function will be a determinant

$$\Psi(1, 2, \cdots n)=\frac{1}{(n!)^{\frac{1}{2}}}\begin{vmatrix}\psi_1(1) & \psi_2(1) & \cdots & \psi_n(1)\\ \psi_1(2) & \psi_1(2) & \cdots & \psi_n(2)\\ \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot\\ \psi_1(n) & \psi_2(n) & \cdots & \psi_n(n)\end{vmatrix} \quad (1)$$

where the numbers in parentheses represent the Cartesian and spin coordinates of the corresponding electrons and the ψ are the wave functions of the different states.[8] In order to obtain the statistical relations between the positions of two electrons we have to square (1) and integrate it over the coordinates of all electrons except those considered, which will be taken as 1 and 2. Because of the orthogonality relations of the ψ_κ the result will be, apart from a constant,

$$\sum_{\kappa=1}^{n}\sum_{\lambda=1}^{n}[|\psi_\kappa(1)|^2|\psi_\lambda(2)|^2-\psi_\kappa(1)\psi_\lambda(1)^*\psi_\kappa(2)^*\psi_\lambda(2)]. \quad (2)$$

This still contains the spin coordinates s_1 and s_2 of 1 and 2 and reads more explicitly, if the edge of the cubic-shaped crystal is L,

$$\sum_{\nu_1\nu_2\nu_3}\sum_{\mu_1\mu_2\mu_3}[|e^{2\pi i(\nu_1x_1+\nu_2y_1+\nu_3z_1)/L}|^2|e^{2\pi i(\mu_1x_2+\mu_2y_2+\mu_3z_2)/L}|^2\delta_{s_1\sigma_1}\delta_{s_2\sigma_2}$$
$$-e^{2\pi i[(\nu_1-\mu_1)(x_1-x_2)+(\nu_2-\mu_2)(y_1-y_2)+(\nu_3-\mu_3)(z_1-z_2)]/L}\delta_{s_1\sigma_1}\delta_{s_1\sigma_2}\delta_{s_2\sigma_2}\delta_{s_2\sigma_1}]. \quad (2a)$$

There are really two questions to discuss: the statistical connection between electrons with antiparallel spin ($\sigma_1=-\sigma_2$) and between those with parallel spin ($\sigma_1=\sigma_2$). For a pair of the first kind the second term of (2a) vanishes so that they are statistically independent. For two electrons with parallel spin, on the other hand, we have to evaluate the sum of (2a) after having omitted the spin factors. We shall denote the distance of the two electrons by r, and may assume that the line joining them lies in the X direction, since the probability will not depend on the direction. With these conditions, (2a) becomes

$$\sum_{\nu_1\nu_2\nu_3}\sum_{\mu_1\mu_2\mu_3}(1-e^{2\pi i(\nu_1-\mu_1)r/L}). \quad (3)$$

Here the summation over ν_2, ν_3, μ_2, μ_3 can be carried out at once. The limitation on the ν_1, ν_2, ν_3 and μ_1, μ_2, μ_3 being

$$\nu_1^2+\nu_2^2+\nu_3^2\leq\nu^2;\quad \mu_1^2+\mu_2^2+\mu_3^2\leq\nu^2$$
$$\nu=(3n/8\pi)^{\frac{1}{3}} \quad (4)$$

it gives

$$P(r)=\sum_{\nu_1=-\nu}^{\nu}\sum_{\mu_1=-\nu}^{\nu}\pi^2(\nu^2-\nu_1^2)(\nu^2-\mu_1^2)(1-e^{2\pi i(\nu_1-\mu_1)r/L}). \quad (5)$$

Now the summation over ν_1 and μ_1, after dividing by $\pi^2\nu^2(4\nu^2-1)^2/9$ gives for the probability of the electrons with parallel spin being a distance r apart

[7] There is nothing like exchange forces in our picture.

[8] This consideration is contained implicitly in the work of Uhlenbeck and Gropper for the case of only slightly degenerated gases, Phys. Rev. **40**, 1029 (1932). We are interested in the case of complete degeneracy, however.

$$4\pi r^2 P(r) = 4\pi r^2\left\{1-\left(\frac{3}{2}\frac{\cos(\pi r/L)\sin(2\pi\nu r/L)-2\nu\sin(\pi r/L)\cos(2\pi\nu r/L)}{\nu(4\nu^2-1)\sin^3(\pi r/L)}\right)^2\right\}$$
$$= 4\pi^2 r^2\left\{1-\left(3\frac{\sin(r/d')-(r/d')\cos(r/d')}{(r/d')^3}\right)^2\right\}. \quad (6)$$

Here $d'=v_0^{\frac{1}{3}}/3^{\frac{1}{3}}\pi^{\frac{1}{3}}$ and $v_0=L^3/n$ is the atomic volume. The function $P(r)$ is sketched in Fig. 2, it vanishes for $r=0$ and approaches 1 as r becomes large compared with the lattice constant. It attains its half-value for $r=1.79\ d'$ or $0.460\ d$ for a body-centered lattice with a cube edge d. The radius of the sphere described above is about the same, namely $(\frac{3}{8}\pi)^{\frac{1}{3}}d=0.492\ d$. So we see that two electrons with parallel spin will be very rarely at the same ion, simply in consequence of the exclusion principle. This will be also true for a Fermi gas subject to a periodic potential, as the potential does not materially alter this argument.

It remains to investigate the case of antiparallel spins somewhat more closely. As it is not possible that three electrons have antiparallel spins, the probability of three electrons being at the same ion will be very small anyway. For two electrons with antiparallel spins and without interaction, however, there is no statistical connection of the positions. If one should take the interaction into account, it would turn out, however, that there is a connection of such a kind that they are but rarely in the neighborhood of each other. This is already indicated in the well-known solution of Hylleraas[9] for He and in the similar solution of Bethe[10] for the negative hydrogen ion. These solutions also show that the connection is of such an order of magnitude that the choice of potential function, which corresponds to our rather rough picture of the metallic bond, is justified to some extent. It must be admitted, however, that the lower limit of the energies of the free electrons, which we calculate in this way, will certainly give too large a binding energy for the lattice, as all of the electrons will not be at different ions with certainty, and also because the terms of Hylleraas and Bethe just discussed will increase the kinetic energy above the value which we obtain by our boundary conditions. We shall not take up this question in more detail this time as it is deeply connected with the interaction problem of the electron and the justification of the notions of the free and bound electrons and we hope to return to it at another time.

IV.

The calculation of the wave function inside the proper spheres of the ions is very simple in principle. The potential function of Prokofjew[11] was used for the purpose. This was obtained by Prokofjew following a method of Kramers[12] in which one employs experimental values of the terms of Na. The differential equation for the radial function $R=r\psi(r)$ is

$$-(h^2/8\pi^2 m)(\partial^2 R/\partial r^2)+V(r)R=ER(r) \quad (7)$$

and in units of the Bohr radius of H, the quantity $Q(\rho)=-a_0\rho^2 V/e^2$, is approximated for various intervals by parabolas, as follows:

$\rho=0.00$	to 0.01	$Q=11\rho$
0.01	0.15	$=-26.4\ \rho^2+11.53\ \rho-0.00264$
0.15	1.00	$=-\ 2.84\ \rho^2+\ 4.46\ \rho+0.5275$
1.00	1.55	$=+\ 1.508\ \rho^2-\ 4.236\ \rho+4.876$
1.55	3.30	$=\ 0.1196\rho^2+\ 0.2072\rho+1.319$
3.30	6.74	$=\ 0.0005\rho^2+\ 0.9933\rho+0.0222$
6.74	∞	$=\rho$

The boundary condition $\partial\psi/\partial r=0$ requires that at the boundary R should satisfy

$$\partial R/\partial r = R/r. \quad (8)$$

[9] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).

[10] H. Bethe, Zeits. f. Physik **57**, 815 (1929).

[11] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929). (Note: Prokofjew's table of $Q(\rho)$ (p. 258) contains obvious errors in two places, one in decimal point and one in sign. These were easily detected by the continuity conditions. The form given here is corrected.)

[12] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926).

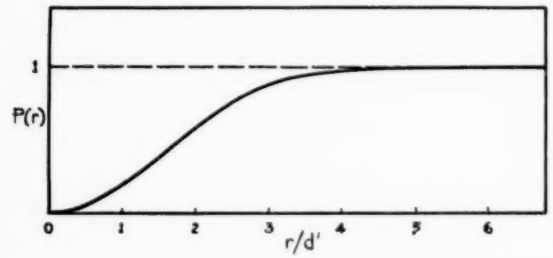

FIG. 2.

Instead of finding the energy value E for different radii of the sphere, the radii corresponding to different energy values were determined. Thus an arbitrary energy value E was taken and the corresponding wave function was obtained from (7) using the method of finite differences employed by Prokofjew. The calculation was started at $r=0$, however, so that every calculated wave function could be used. For $r=0$ the radial function R vanishes and the solution up to $r=0.025$ was calculated by means of a power series in r. After this the method of finite differences was employed, first with differences of 0.005 and then with larger ones when allowable. The largest difference employed was 0.32 ($r>4.6$). The wave function had practically no dependence on E in the neighborhood of the origin so that it was not always necessary to repeat this part of the calculation. As a check, the energy of the electron in the free atom was also determined, the calculated value lies between 0.3820 and 0.3800 Rydberg units, while the experimental value is 0.3778. In Fig. 3, the wave function of the free atom and the wave function for $E=0.500$ are plotted. The numerical tables will be published at another time.

After having the wave function, it was easy to determine the radius of the sphere, for which the boundary condition (8) is satisfied by drawing the tangents to R from the origin. The figure shows, that the boundary conditions are satisfied for two different radii, so that every numerical integration yields two points of the $E(r)$ curve, which gives the energy of the most strongly bound free electron as a function of the lattice constant $d=(8\pi/3)^{\frac{1}{3}}r$. In Fig. 4 the $E(r)$ curve is given (lower line), the unit of energy being the ionization energy of H. For very large r it approaches the ionization energy of atomic Na, possesses a minimum around $r=3$, and rises again for smaller values of r. This latter behavior is due to the fact that a further compression of the lattice would push the valence electron inside the closed L shell, which of course requires energy. The lattice, unlike a similar H lattice,[13] would be stable, therefore, even without taking into account Fermi statistics.

The calculation of a wave function took about two afternoons, and five wave functions were calculated on the whole, giving the ten points of

[13] Cf. E. A. Hylleraas, reference 3.

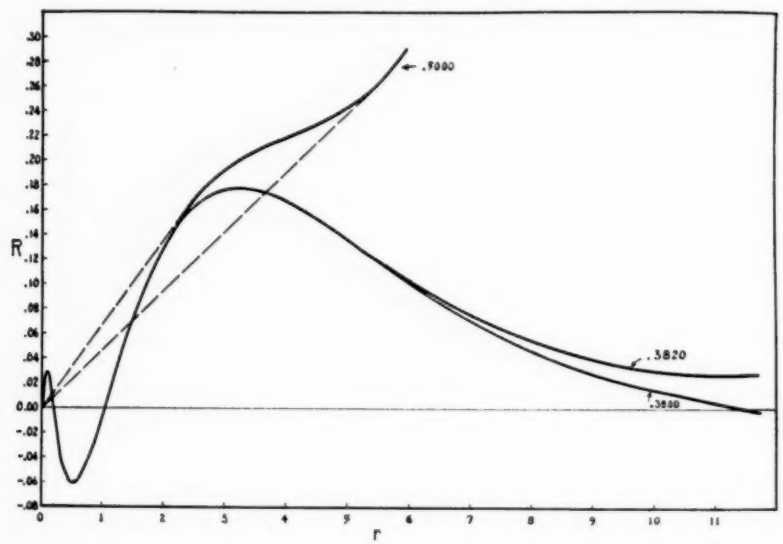

FIG. 3.

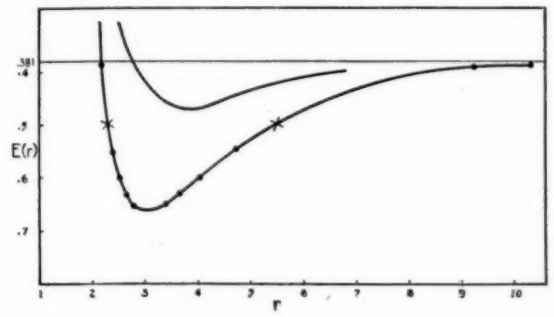

FIG. 4.

the figure. The points of the wave function of Fig. 4 are marked by a cross.

Another point which should be mentioned is that concerning the change in energy of the inner shells. The change is not due chiefly to the change of the boundary conditions as discussed above for the valence electron. This, of course, does increase the binding energy of these electrons, but only by a very small amount. A greater change arises from the increase in the probability of the valence electron being inside the L-electrons, because of the material change of the normalization factor. This decreases the binding energy of the inner electrons and hence lowers the heat of vaporization. A calculation of this effect has been made and shows that the decrease in binding energy is 0.008 Rydberg units per atom, or 2500 small calories per mole. This was obtained by evaluating the change of the potential of the inner electrons in the field due to the valence electron for the free and bound atom. The inner charge distribution was taken to be that given by Hartree.*

V.

The last question we have to investigate is concerned with the additional energy of the other free electrons due to the Fermi distribution. This energy was calculated by the simple Fermi formula and it gives a mean additional energy for every electron

$$\frac{3h^2}{10m}\left(\frac{3}{8\pi}\right)^{\frac{2}{3}}\frac{1}{V_0^{\frac{2}{3}}}=\frac{9h^2}{80\pi m}\left(\frac{3}{2\pi}\right)^{\frac{2}{3}}\frac{1}{r^2} \qquad (9)$$

or $(9\pi/10)(3/2\pi)^{\frac{2}{3}}r^{-2}$ if the energy is measured in Rydberg units and r in Bohr units. As a matter of fact, this formula is valid only for free electrons and it certainly gives too large a value for bound electrons. The fact that the energy differences for bound electrons are smaller than for free electrons was shown first by Bloch.[14] It also follows from the following argument. Let the wave function of the electron with the lowest energy be $\psi_{000}(x, y, z)$, which is invariant with respect to an addition of an identity period to the coordinates. This invariance is not possessed by the wave functions of the other free electrons, and that with the quantum numbers ν_1, ν_2, ν_3, will be multiplied by $e^{2\pi i\nu_1 d/L}$, $e^{2\pi i\nu_2 d/L}$ and by $e^{2\pi i\nu_3 d/L}$ if x, y, or z are increased by d, respectively. Now ψ_{000} gives the lowest possible energy of all wave functions, which are orthogonal to the wave functions of the L and K shells. For the wave function with the quantum numbers ν_1, ν_2, ν_3 this is true if we compare it only with functions which have the same symmetry character, i.e., are multiplied by the same factors if one replaces x, y or z by $x+d$, $y+d$ or $z+d$, respectively. There is, however, the function

$$\psi_{\nu_1\nu_2\nu_3}=e^{2\pi i(\nu_1 x+\nu_2 y+\nu_3 z)/L}\psi_{000}(x, y, z), \qquad (10)$$

which has all the required properties and the energy of which differs from that of ψ_{000} only by $(h^2/2mL^2)(\nu_1^2+\nu_2^2+\nu_3^2)$, the Fermi energy for free electrons. This is easily seen upon calculating $(\psi_{\nu_1\nu_2\nu_3}, H\psi_{\nu_1\nu_2\nu_3})$ for (10) and remembering that ψ_{000} may be assumed to be real. The energy of the real wave function with the quantum numbers ν_1, ν_2, ν_3 is certainly less than that of (10) and so the average additional energy for the free electrons in higher states is also certainly less than (9). Nevertheless (9) was adopted in the subsequent calculation and the corresponding expression added to the energy of the lowest electron $E(r)$. The result is given in Fig. 4 (upper line). It is probably true that the fact that (9) gives a too high value largely compensates the error which was made by the assumption of the free electrons, as discussed in Section III.

VI.

The upper curve in Fig. 4 gives at once all quantities we desire to calculate. The position of the minimum gives the radius of the sphere for which the energy is the smallest and

* Hartree, Proc. Camb. Phil. Soc. **24**, 111 (1927).

[14] F. Bloch, Zeits. f. Physik.

when multiplied by $(8\pi/3)^{\frac{1}{3}}$ it should give the lattice constant for the absolute zero point. Similarly the depth of the minimum below the line of the energy for the free atom should give, after subtracting the correction for the energy gained by the inner shells (2.5 kilo cal.) the energy difference between the gas and the solid state (i.e., the heat of vaporization per atom) in Rydberg units at the absolute zero point. Finally the curvature at the minimum r_m is in a simple connection with the compressibility: the energy change for a linear compression in the ratio α per volume v_0 is $v_0\kappa(3\alpha)^2/2$, where κ is the compressibility, and, on the other hand, it is $\frac{1}{2}r_m^2\alpha^2 d^2E(r_m)/dr^2$ when calculated from the figure. This gives

$$\kappa=(1/9)(r_m^2/V_0)(d^2E(r_m)/dr^2). \qquad (11)$$

The quantity d^2E/dr^2 was calculated as if the lower curve were linear at r_m and all the curvature arose from (9), which is approximately true according to the figure. The final values obtained for the three quantities d, λ and κ are $d=4.2$A, $\lambda=25.6$ kilo cal./mol, $\kappa=1.6\times10^{-11}$ c.g.s. The depth of the minimum of the lower curve below the energy of the free atom is 88.5 kilo cal.; and the depth at the point where the upper curve has its minimum is 70.4. The Fermi correction at this point is 42.3 kilo cal. In order to have a fair comparison with experiment, the experimental values for these quantities must be extrapolated to the absolute zero point. It must be remembered, however, that we did not treat the motion of the nuclei by quantum mechanics and in consequence, the extrapolation should be done in such a way as to neglect the quantum effects. This was done by taking the values for room temperature and correcting them linearly. The three values for room temperatures are[15]: $d=4.30$A; $\lambda=26.00$ kilo cal./mol; $\kappa=1.67\times10^{-11}$ c.g.s. The coefficient of thermal expansion is 62×10^{-6};[16] the corrected value of λ is determined by adding the difference in heat content of solid and gas ((6−3) cal./deg.$\times$300 deg. = 900 cal.) to the room temperature value of λ; and the value of κ at 0°K was obtained by extrapolating values given along with the above. The final values are: $d=4.23$A, $\lambda=26.9$ kilo cal./mol; $\kappa\sim1.0\times10^{-11}$ c.g.s. The theoretical values compare favorably with these, partly, without doubt, as a consequence of compensating errors.

The work on sodium is being extended with particular reference to a more exact determination of the distribution of energy levels in the neighborhood of the lowest one. Moreover, the corresponding calculations on Li, K, Rb, by using Hartree's and Hargreaves' fields,[17] are being undertaken by one of us.

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[15] d: P. P. Ewald, Hand. d. Phys. XXIV, 331.
λ: J. Sherman, Chem. Rev. **11**, 93 (1932).
κ: Landolt Bornstein, Erster Ergaenzungsband 5 auf., 25. Int. Crit. Tables III, 47.

[16] Int. Crit. Tables II, 461.

[17] We wish to offer our thanks, at this time, to Professor J. C. Slater and hence to Dr. Hartree, for the use of the unpublished tables of K^+.

Photoelectric Sensitivity of Magnesium

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The photoelectric sensitivity of gas free surfaces of magnesium deposited on glass has been determined in the visible region of the spectrum. The long wave limit for all such surfaces deposited in vacuum is approximately 5100A. Air or oxygen in small amounts, or nitrogen activated by a glow discharge, sensitizes the surface to light of longer wave-lengths. Further oxidation of the surface causes the threshold to shift into the ultraviolet region of the spectrum.

A DEPOSIT of magnesium metal on glass is commonly used in the manufacture of certain types of commercial photo-cells. The cathode is prepared by condensing a small amount of the vapor of an alkali metal, which has been carefully purified by distillation in high vacuum, upon an undercoating of magnesium. Caesium cells constructed in this fashion are especially suitable for use in the visual region of the spectrum.[1] In most reports on the use of magnesium undercoatings no mention is made of the photoelectric properties of the magnesium itself, and no extended investigation seems to have been made of the effect of possible variations in the surface structure of the undercoatings on the spectral response of the sensitized cathode in such cells.

In the course of a preliminary investigation of magnesium coatings upon which other metals were to have been deposited, it was found that the magnesium itself was sensitive to visible light. The effect was reproducible and the thresholds the same for all coatings formed by slow vaporization of the metal, although previous coatings "flashed" by means of an induction furnace had not responded uniformly to visible radiation. An extension of the study to include the effect of various gases has shown that small amounts of oxygen render the surface more sensitive to red light, while a thorough oxidation of the surface destroys its response to visible light. Nitrogen, on the other hand, exhibits no effect except when activated by means of a glow discharge within the cell. The results obtained appear to confirm the hypothesis that the thresholds usually assigned to magnesium, which lie between 3300A and 3800A, are not those characteristic of the pure metal, but are due to contaminated magnesium surfaces.

[1] Zworykin and Wilson, J.O.S.A. and R.S.I. **19**, 81–89 (1929).

EXPERIMENTAL PHOTO-CELLS

Fig. 1 shows one form of cell employed in the present experiments. Pieces of chemically pure magnesium ribbon, or magnesium turnings, were packed into a small nickel or molybdenum cylinder, usually about 12 mm long and 5 mm in diameter and closed at one end. This was attached to an isolantite heating element through which passed a hairpin tungsten filament. *M* is the cylinder containing the magnesium, with opening at *O*. *A* is a nickel wire loop which

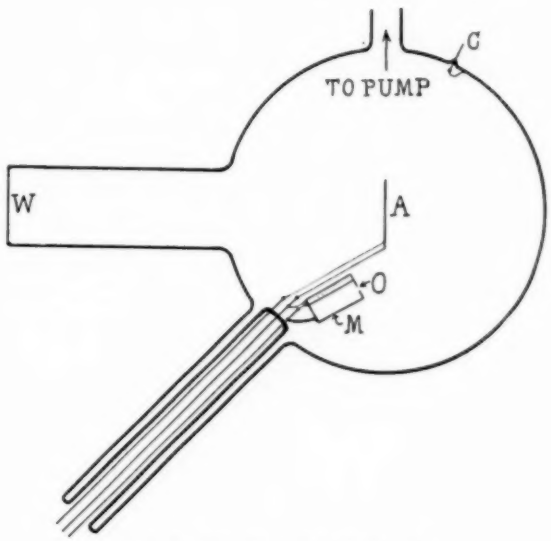

FIG. 1. Experimental photo-cell.

serves as a central anode, and which can be separately heated. *W* is a plane Pyrex window sealed to the bulb, through which light is admitted to the cell. *C* is the cathode lead, and is a tungsten wire sealed through the glass wall and spot welded to a platinum wire which was fused to the inner surface of the bulb for the purpose of making intimate contact with the magnesium coating.

After a cell was sealed on to the pumping system, the metal parts were heated by means of an electric current, and in the later cells, hydrogen was allowed to circulate through the system for about one hour. Each cell was then baked for a period of from 12 to 36 hours in an electric oven at a temperature of 400°C, and evacuated by means of a single stage mercury diffusion pump and Cenco backing pump. Tests for residual gas were made by means of a spark coil, and by observation of the photoelectric emission from the deposited coating. The system contained two liquid air traps and a mercury cut-off in order that a cell could be isolated and observed over a period of several days or weeks.

Magnesium was distilled slowly from the cylinder after the outgassing process was comp'eted, until a heavy mirror coating was deposited upon the Pyrex bulb. All coatings formed in this manner were sensitive to visible light. A spectral response curve was determined for each new surface formed, and the distillation was repeated several times. Sensitivity readings for surfaces which had remained under high vacuum conditions for periods up to fifty hours showed no observable change in the threshold. In some cases the total emission increased slightly with time, finally settling down to a stable value.

Apparatus for Determining Photoelectric Sensitivity

Photocurrents obtained when the magnesium was illuminated by a Mazda test lamp were measured with a Leeds and Northrup galvanometer having a sensitivity of 2.05×10^{-11} amp. per mm. Emission currents obtained with resolved light were measured by means of an FP 54 Pliotron amplifier,[2] a Weston microammeter being used in the plate circuit. The approximate value of unit current on the scale used for most of the photoemission plots in this paper is 1×10^{-13} amp.

A Hilger glass monochromator was used in determining the spectral sensitivity of the magnesium coatings. Light from the linear spiral filament of a 68 watt tungsten lamp was focussed on the collimator slit of the instrument. A slit width of approximately 0.5 mm was used throughout these tests. The energy distribution of the resolved light was determined by means of an improved form of Nichols radiometer.[3]

Long Wave Limit for Magnesium Coatings Deposited in Vacuum

Currents obtained with cell I were originally assumed to be due to impurities on the magnesium surface, a maximum in the total emission plot occurring at 4500A. The results obtained with a second cell, however, were substantially the same, as were those of all subsequent coatings deposited under conditions of a high vacuum in bulbs which had been thoroughly baked and outgassed. The variation in photoemission with wave-length for magnesium coatings deposited in cell II is shown in Fig. 2. Readings of the microammeter in the Pliotron circuit are plotted as ordinates, wave-lengths of resolved light as abscissae. This cell was baked for 36 hours, but was not treated with hydrogen. A window was formed by applying a small flame to the bulb. The long wave limit lies at approximately 5200A.

The second set of emission curves for magnesium coatings deposited in vacuum is given in Fig. 3. Two separate coatings were made with the cell continuously on the pumping system, and in each case the vaporization of the magnesium was allowed to proceed very slowly over a period of from two to three hours. This cell was not given a preliminary hydrogen treatment, and windows were made by flaming the coating from a small area of the bulb. Within the limits of experimental error the long wave limit for these coatings falls at 5100A.

A large number of observations were carried out by using cell V, the construction of which is shown in detail in Fig. 1. Since a side window was provided upon which very little magnesium was

[2] L. A. DuBridge, Phys. Rev. **37**, 392–400 (1931).

[3] B. J. Spence, J.O.S.A. **6**, 625–28 (1922).

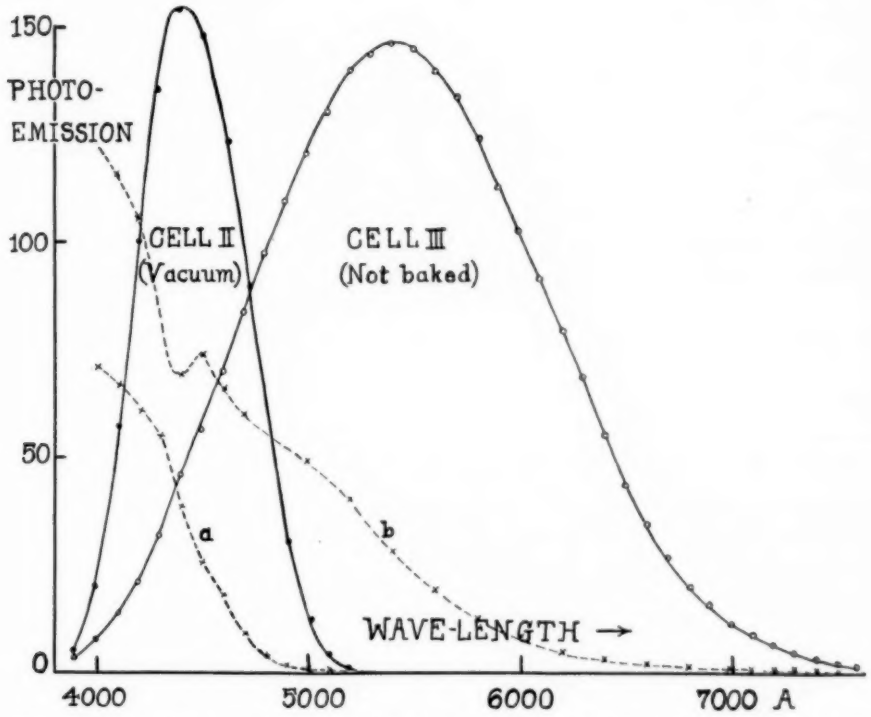

FIG. 2. The solid curves show the total photoemission plotted as a function of the wavelength of light from the monochromator. Curves *a* and *b* are the corresponding emissions per unit of radiant energy.

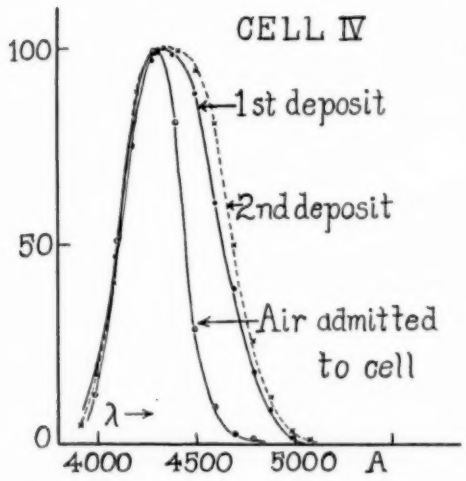

FIG. 3. Total emission curves for two magnesium coatings deposited under conditions of high vacuum, and for one coating after exposure to a small amount of air. The ordinates for these plots, as well as those for Fig. 4, are adjusted to make the maximum readings the same.

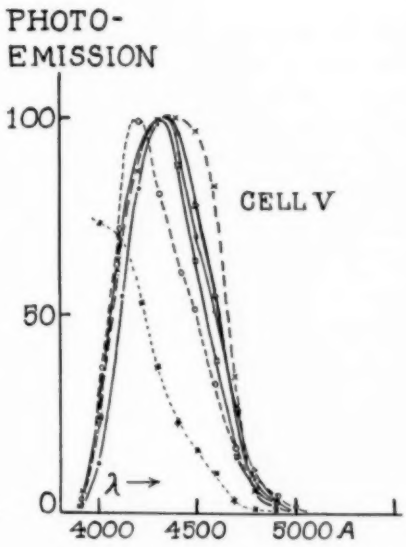

FIG. 4. Total photoemission curves for new coatings in cell V. Dots indicate initial deposit; crosses, two subsequent deposits in vacuum; circles, deposits after air was admitted; triangles and squares, heavy deposits following admission of O_2. The remaining curve shows photoemission per unit radiant energy computed for the initial heavy deposits.

deposited, it was possible to repeat the distillations many times. Spectral response curves were determined for each of six new coatings deposited at intervals while the pumps were in operation, during the course of several weeks of observation. These curves are shown in Fig. 4, ordinates being adjusted so that the value of maximum emission is the same for all. The long wave limit for each of these coatings is approximately 5000A.

It is to be noted that the thresholds for the earlier cells lie some 200A farther to the red end of the spectrum than those for cell V. This discrepancy is larger than the estimated error of measurement, and is probably due to the fact that in the previous cells traces of gas were released when the windows were flamed. On the whole, the measurements taken on ten magnesium coatings are in fair agreement in fixing the long wave limit at about 5100A. Additional information as to the nature of these freshly distilled surfaces is furnished by the tests described in the sections below, which deal with the effect of gases on the photoelectric sensitivity.

Effect of Air on Photosensitivity

That alkali metal surfaces may be sensitized by the application of various gases and vapors has been known since the time of the early experiments by Elster and Geitel. In order to test the possible effects of poor cleaning and evacuation, a cell was made through which hydrogen was not passed, and which was not baked in the electric furnace. After pumping and sealing off the bulb, magnesium was vaporized by heating the cylinder and a heavy coating deposited upon the walls of the tube. A window was formed by flaming a clear spot on the side wall. Tests on the variation of photocurrent with potential showed that the cell was gassy. Fig. 2 shows a spectral response curve for this cell (cell III) with an accelerating potential of 240 volts. Although the long wave limit lies at about 7500A, the efficiency of the cell is very small by comparison to a Cs-Mg gas photo-cell. Duplication of this type of surface by direct application of gases, or by means of glow discharges set up within the cell, has so far been impossible, and it is believed that this extreme sensitization to red light is due to the release of air and possibly water vapor from the unbaked glass walls.

An attempt was made to determine the effect of air upon the sensitivity of the second coating deposited in cell IV. The admission of air at a pressure of less than 0.5 of a micron resulted in an initial increase in the emission, followed by a considerable decrease, and the cell was immediately evacuated by means of the diffusion pump. The spectral response of the coating was then measured, the readings being shown in the third curve of Fig. 3. When air was admitted a second time, the emission fell to a value too small to be detected.

The study was continued by admitting still smaller amounts of air to cell V. The oxygen content of the air was considerably reduced by bubbling it through a solution of pyrogallic acid and potassium hydroxide. The results are shown in Fig. 5.

Curve *A*, of Fig. 5, gives the emission obtained from the second coating of magnesium plotted as a function of the wave-length of incident light. Curve *B* indicates a similar test after air had been admitted and pumped out. Curve *C* shows the increase in emission and in red sensitivity of the coating produced by admitting a second dose

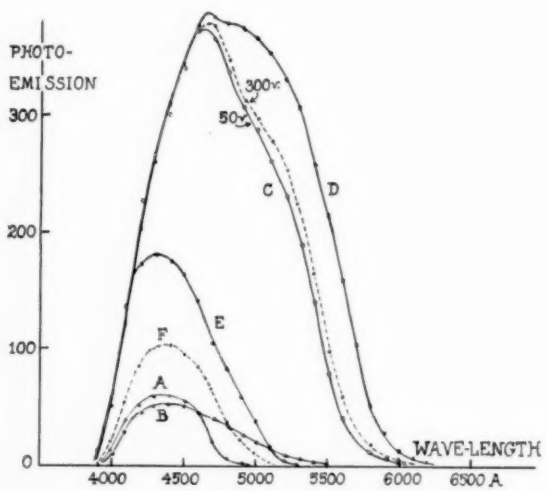

Fig. 5. Sensitization of a magnesium surface by contact with air. Curve *A* shows sensitivity of the coating as deposited in vacuum; *B*, sensitivity after first dose of air; *C*, sensitivity after second dose. *D* shows the effect of depositing a minute amount of magnesium upon the gas contaminated surface, *C*. *E* and *F* show the effects of further heavy magnesium deposits. The amplitudes shown are only rough approximations of the relative response of the various surfaces.

of air and leaving it continuously in contact with the surface for a period of 72 hours. This test was followed by a very slow heating of the magnesium cylinder in an effort to determine the effect of a deposit of a thin film of the metal upon an oxidized undercoating. Curve *D* shows the result of what was regarded as the maximum sensitization procurable by this process. A fourth deposit of the metal resulted in an immediate decrease in total emission, and response curve *E* shows that the long wave limit has shifted from a maximum at 6300A to about 5300A. Further deposits of magnesium in the presence of the residual gas indicated that the new surface was similar to that formed by initial deposits in high vacuum, the long wave limit finally decreasing to 5100A, as shown by curve *F*. The gas pressure likewise was found to be decreasing somewhat during this time, and a glow discharge indicated the presence of nitrogen only within the cell.

Effect of Oxygen on Photosensitivity

The influence of small amounts of oxygen admitted to cell V is shown in the plots of Fig. 6. Curve *A* shows the response for a freshly deposited surface formed after the cell had been thoroughly evacuated following the tests with air. The vacuum system up to the mercury cut-off was flushed several times with thoroughly dried tank oxygen, and the pumps allowed to operate until the pressure was very low on the high vacuum side of the diffusion pump. The mercury cut-off was then lowered, but no effect was observed in the photoemission.

A small amount of oxygen gas at approximately 0.01 mm pressure was trapped in a volume of about 100 cm³ in the tube joining forevacuum pump and the mercury pump. The diffusion pump was then shut off and the gas allowed to diffuse up to the mercury cut-off. The cut-off was then lowered slightly for an instant, the result being an immediate increase in the photoemission produced by the test lamp. Readings taken with resolved light showed some increase in red sensitivity. A second momentary opening of the cut-off resulted in a three-fold increase in photocurrent, and it was evident that more than enough oxygen had been admitted than that required to give maximum sensitization. The data on the spectral sensitivity produced are given by curve *B* of Fig. 6. The cut-off was permanently lowered, and curve *C* shows the spectral response obtained after the surface had been exposed to the action of the oxygen for a period of 36 hours, after which

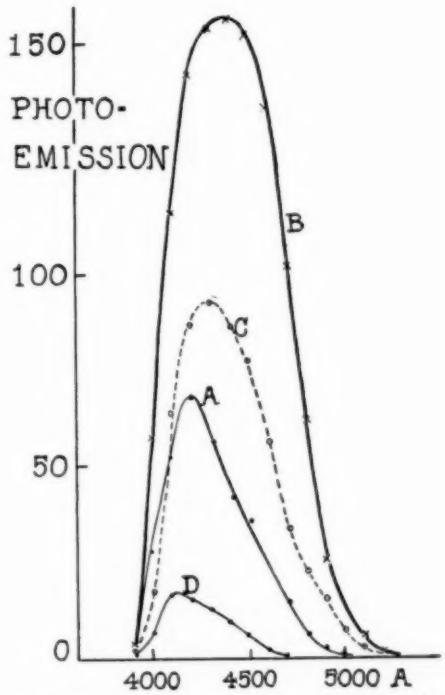

Fig. 6. Effect of O_2 on sensitivity of magnesium coating. *A*, coating deposited in vacuum. Curve *B* shows effect of admitting a trace of O_2; curve *C* indicates the effect of a second dose of gas, while *D* shows the decrease in sensitivity produced by a third treatment.

time spark coil tests showed that the oxygen had been completely cleaned up.

The entire procedure described above was then repeated, the final result being illustrated by curve *D*, the response to visible light now being very small. A third dosage of oxygen lowered the response to visible light to such a point that no emission could be detected. By placing a quartz mercury arc directly in front of the cell window, however, it was found that the oxidized surface responded to emission lines in the ultraviolet which were not absorbed by the Pyrex. A deflection of about 7 mm with the high sensitivity galvanometer was obtained in this manner. It thus appears that an oxidized magnesium surface has a threshold somewhere below 4000A, the

limit of the visible spectrum tests, and above 3650A, the only intense line in the ultraviolet spectrum of mercury that is transmitted by Pyrex. Since further oxidation did not destroy this response to the light from the arc, it seems very probable that the long wave limit for oxidized magnesium is approximately 3800A.

Effect of Nitrogen on Photosensitivity

The cell was evacuated and fresh surfaces of magnesium were deposited following the test with oxygen, plots for these surfaces being included with those shown in Fig. 4. The entire vacuum system up to the cut-off was then washed out several times with nitrogen which had been completely freed of oxygen and dried. Results of the tests with N_2 are shown in Fig. 7. The lower amplitude for curve *B* showing the emission from the surface following the second deposit is due to a slight fogging of the window caused by the vaporized magnesium. Curves *C* and *D* show the results of admitting nitrogen to the photo-cell. Curve *E* is a plot of *B* multiplied by a factor 7.2, and shows that the gas acts merely to amplify the photocurrents, the spectral sensitivity and long wave limit being essentially the same for *D* as for *B*.

When a glow discharge is set up in nitrogen, however, the emitting surface is changed, probably by the formation of magnesium nitride.[4] Another possibility, although a doubtful one, is that the sensitivity at 5100A of a new surface is due to an adsorbed gas layer which is removed by the electric discharge. The spectral response of the surface following this treatment is given by curve *F* of Fig. 8, which shows a shift in the long wave limit from 5000 to 5400A. Additional glowing of the gas did not seem to increase further the sensitivity of the surface, a prolonged and rather heavy discharge eventually destroying the response to visible light. A further investigation of the change in photoelectric properties of magnesium when a glow discharge is set up should be valuable in obtaining information as to the manner in which magnesium cleans up various gases when used as a "getter" in vacuum tubes. (See also Fig. 9.)

[4] Lukirsky and Ptizyn, Zeits. f. Physik **71**, 339-49 (1931).

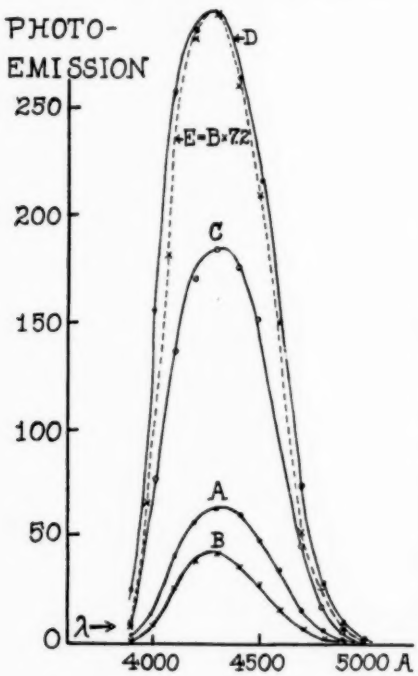

Fig. 7. Effect of nitrogen upon the photosensitivity of magnesium coatings. The long wave limit is not changed when gas is admitted.

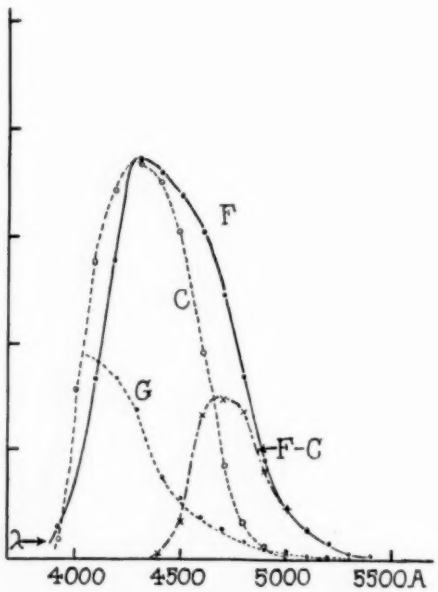

Fig. 8. Curve *F* shows the increase in red sensitivity of magnesium caused by a glow discharge in N_2. *G* is the emission per unit energy corresponding to the total emission curve *F*. *F*−*C* is the difference between *F* and *C*.

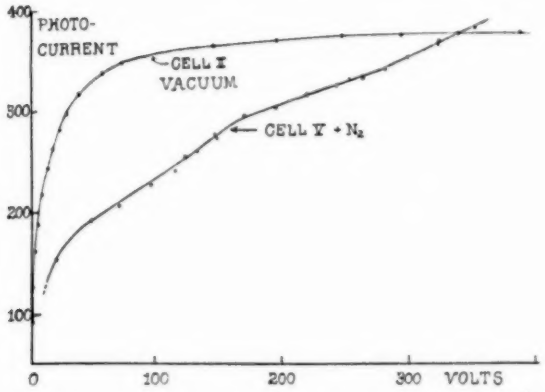

FIG. 9. Current-potential plots for a vacuum cell (II), and for cell V after admitting nitrogen gas.

DISCUSSION OF RESULTS

The deposition of magnesium by careful distillation in a good vacuum, results in a surface which has a long wave limit of approximately 5100A. If the photoelectric properties of such coatings are determined by the formation of a compound surface, or by the adsorption of a gas layer, then these properties might be expected to vary considerably from cell to cell as conditions of heat treatment and evacuation are varied. But within the limit of error of the measurements the same threshold was found for repeated distillations in the same cell, and for new deposits from different magnesium samples in several cells. Moreover, if the active surface layer is one formed of a stable compound the repeated formation of which is not hard to attain, then one should not expect slight additions of O_2, or of active N_2 formed in a glow discharge, to further sensitize the surface as has been found in these experiments.

It is interesting to compare the results of the present experiments with those obtained by other investigators. Pohl and Pringsheim[5] found a continual increase in photosensitiveness of distilled magnesium surfaces with time over a period of 24 hours, the long wave limit in one instance increasing to approximately 7000A. In the present investigation the increase in photoemission under standard test conditions was less than 12 percent over a period of 54 hours in the case of cell V, and there was no appreciable change in the long wave limit while the cell was isolated with liquid air trap between cell and mercury cut-off. Moreover, no decrease in emission was noted in these freshly deposited coatings. Absence of fatigue may be taken as indicating the absence of gas layers on the metal surface.[6] It has been the experience of many investigators that denuding a surface of gas shifts the long wave limit to the red end of the spectrum.[7] Others have shown an initial sensitization to red light, probably due to the adsorption of a monomolecular layer of gas, and an eventual shift of threshold to shorter wave-lengths (or at least a marked decrease in emission) with additional adsorption of gas.[8]

The authors believe their results on the effect of gases are to be explained in terms of the formation of a surface compound of magnesium. If this is true the early results for magnesium metal scraped with a steel tool under vacuum conditions which were obviously poor in all probability gave a long wave limit not characteristic of a clean magnesium surface, but one which is characteristic of magnesium oxide. This contention is of course supported in a definite way by the present tests on the response of an oxidized surface to the radiation from a mercury arc.

Recent reports on the photoelectric properties of magnesium deposited in various ways seem to lend support to the above interpretation, when account is taken of working conditions and methods used. For layers *sputtered* in an atmosphere of inert gas, it is quite certain that the coating formed will contain most, if not all, of the magnesium compounds existing in the original sample. Results obtained by Rentschler, Henry and Smith[9] for magnesium surfaces prepared in this manner indicate a threshold at 3700A in good agreement with that obtained by many observers for the bulk metal scraped in vacuum. Locher,[10] not attempting to work under conditions of a high vacuum, found a long wave limit for MgO on Mg somewhere between 3400

[5] Pohl and Pringsheim, Verh. d. Deutsch. Phys. Ges. **14**, 546 (1912); **15**, 111 (1913).

[6] L. W. Morris, Phys. Rev. **37**, 1263–68 (1931).

[7] R. P. Winch, Phys. Rev. **37**, 1269–75 (1931).

[8] S. Rijanoff, Zeits. f. Physik **71**, 325 (1931).

[9] Rentschler, Henry and Smith, Rev. Sci. Inst. **3**, 794–802 (1932).

[10] Locher, Phys. Rev. **42**, 534 (1932).

and 4000A, again in approximate agreement with the results of previous workers.

When great care is taken to obtain a pure surface in high vacuum, it has been shown by at least two recent observers that magnesium responds to visible radiation. For relatively gas-free magnesium surfaces deposited upon thoroughly outgassed tungsten, Kenty[11] reports a work function of less than 3 volts, or a long wave limit which is greater than 4100A. The threshold was located approximately by the method of filters with quartz mercury lamp as source. De Laszlo[12] has investigated the photoelectric sensitivity of magnesium films deposited on glass from samples of the metal which previously had been distilled in high vacuum. A quartz monochromator was used with a mercury arc as source. His sensitivity curve indicates a long wave limit for magnesium lying somewhere between 4500A and the long wave limit for lithium, which falls well beyond 5000A. He concludes with the statement that the photoelectric efficiency of magnesium is exceptionally high between 2800A and 2400A, and that it would be of practical use as far out as 4000A.

[11] Carl Kenty, Phys. Rev. **43**, 776A (1933).
[12] H. de Laszlo, Phil. Mag. **13**, 1171 (1932).

Conclusion

These experiments on magnesium coatings show that the photoelectric threshold for layers deposited by slow distillation in high vacuum falls in the visible region of the spectrum. The measured long wave limit lies in the range 5000 to 5200A. The formation of a light surface film of magnesium oxide, or nitride, sensitizes the metal to light of longer wave-lengths, a result which has been observed in the case of the alkali metals. With continued oxidation the sensitivity of the coating to visible light decreases, and tests show that for well oxidized magnesium the threshold lies in the neighborhood of 3800A.

A Multiple Interferometer for Analyzing the Vibrations of a Quartz Plate

H. OSTERBERG, *Department of Physics, University of Wisconsin*

(Received March 23, 1933)

A multiple interferometer, by means of which the various types of vibrations in piezoelectric plates can be determined with a certainty far greater than has hitherto been afforded by other methods, is described and illustrated. This interferometer combines in a convenient form six interferometers for measuring the relative motion of any two plane surfaces of the vibrating plate. A simple analysis of the measurement reveals the type of vibration. The application of this interferometer to the study of rectangular quartz plates is illustrated by photographs from two interesting and enlightening patterns appearing in a square plate of X-cut. These patterns have previously been studied by R. B. Wright and D. W. Stuart with the aid of lycopodium powder. They appear to be formed by two compressional wave trains propagated in opposite directions in the plane of the plate and incident at angles much different from 90° upon the crystal boundaries. The directions of maximum and minimum outward displacement of the end faces are often those in which Young's modulus assumes a critical value. The actual form of these patterns is undoubtedly affected by the anisotropy of Young's modulus. Efforts to determine the above wave trains with the aid of Huyghen's construction have not yet been successful. However, it appears that this construction is capable of explaining why simple longitudinal patterns, of the open ended organ pipe variety, have never been observed by the writer in the ordinary X-cuts.

INTRODUCTION

IT is well known that a plate possessing piezoelectric properties may be caused to vibrate in a variety of modes by applying to the plate in a suitable manner an alternating voltage of appropriate frequency. Much reliable information about the displacements in these modes can be gained with the aid of a simple interferometer in which interference fringes are formed by reflection from the plane quartz surface under observation and an auxiliary surface of glass. The pattern of nodes and antinodes for the component of displacement normal to the surface is made directly visible. The corresponding amplitude can be measured to about one-tenth of the wave-length used for illumination.

In a triple interferometer arrangement which has been recently described[1] the interference pattern formed by reflection from any two parallel surfaces of a quartz plate is compared with the interference patterns formed by reflection from either of these opposing surfaces and an auxiliary fixed surface of glass. With this instrument it is possible to determine the relative displacement of the opposite surfaces. The longitudinal and flexural modes are easily and beautifully differentiated. The instrument is more useful in studying the type of vibration than the simpler interferometer.

There are, however, numerous modes in a rectangular plate which cannot be described to any degree of completeness until the relative motion of any two adjacent surfaces is also known. Fortunately, the triple interferometer arrangement can be simply modified so as to form interference patterns by reflection from two surfaces of the quartz plate which are at right angles as well as from two opposite surfaces. This interferometer, referred to as the "multiple interferometer," combines in a convenient form two optical arrangements, I and II, for determining respectively the relative motion of opposite and adjacent surfaces.

ARRANGEMENT I

This triple interferometer is shown schematically in Fig. 1. A monochromatic beam of light incident upon the half silvered mirror A is divided into beams ab and af. These two beams are in turn divided by the half silvered mirrors C and H. The necessary compensating glasses are B, E and G. D and I are the auxiliary returning mirrors. The quartz plate whose right and left surfaces are under observation is placed at Q. S_1, S_2,

[1] H. Osterberg, J.O.S.A. **23**, 30 (1933).

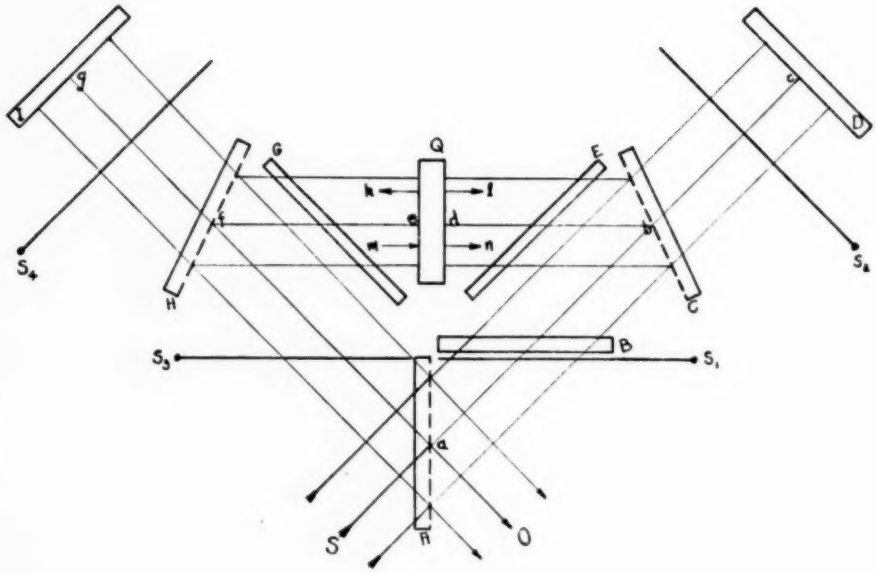

FIG. 1. Schematic diagram of interferometer in arrangement I.

S_3 and S_4 are shutters which may be operated quickly and smoothly.

When S_2 and S_4 are closed and S_3 and S_1 opened, an interference pattern formed by reflection of the beams *abd* and *afe* from the two opposite quartz surfaces is seen by an observer at O provided A, C, Q and H are properly adjusted. This interferometer will be denoted as I (1). When S_3 is closed and S_1 and S_2 opened, the interference pattern seen at O is formed by the reflection of the beams *bc* and *bd* from the mirror D and the right quartz surface, respectively. This is interferometer I (2). Similarly, when S_1 is closed and S_3 and S_4 opened, the pattern viewed at O is formed by reflection of the beams *fe* and *fg* from the left quartz surface and the mirror I, respectively. This interferometer is called I (3).

Suppose that in the adjustment of I (1) the images of the right and left surfaces of Q are so superimposed that opposing particles on those surfaces are brought into coincidence and consider the differences produced in the fringe disturbances of I (1), I (2) and I (3) by two steps of vibration one of which causes the opposing particles to move as indicated by the arrows *l* and *k* and the other of which causes these particles to move as indicated by *n* and *m*. Both optical paths *db* and *ef* are simultaneously shortened by the type of motion described by *l* and *k*. Consequently, no fringe disturbance is caused in I (1) provided the amplitudes of vibration of the opposing particles are equal. In general, smaller amplitudes of vibration are seen in I (1) for this type of motion than in either I (2) or I (3). On the other hand, I (1) shows greater amplitudes of vibration than either I (2) or I (3) for the type of motion described by the arrows *n* and *m*. These two types of relative motion are therefore distinguished by a simple comparison of the amplitudes of vibration revealed by the three interferometers. The measurement of amplitudes of vibration with an interferometer has been discussed in an earlier paper.[2]

ARRANGEMENT II

In this arrangement (Fig. 2) the group consisting of the dividing mirrors A, C and H, the returning mirrors D and I, the compensating glass B, and the shutters is left in the same position as in Fig. 1. H and C are rotated into parallelism with A. The quartz plate is placed at Q with its two surfaces *pq* and *pr* perpendicular to *bd* and *ef*, respectively.

Interference fringes are formed by the beams reflected from *pq* and *pr* by opening S_1 and S_3, closing S_2 and S_4, and adjusting C, Q and H.

[2] H. Osterberg, J.O.S.A. **22**, 35 (1932).

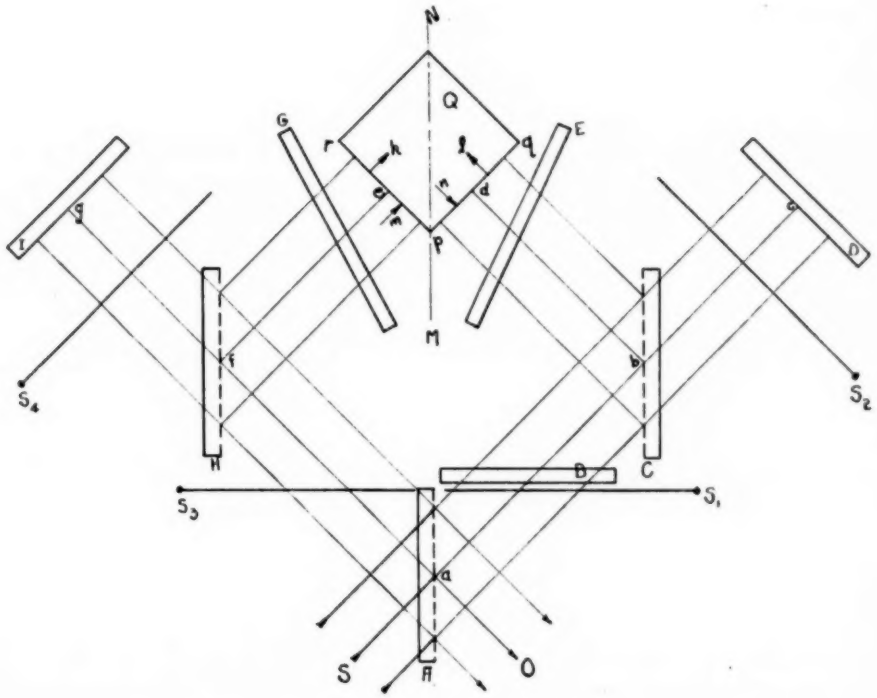

FIG. 2. Schematic diagram of interferometer in arrangement II.

In performing this adjustment C and H are first placed along bf in such a manner that angle fab is approximately a right angle. Q is next arranged such that bd is approximately equal to ef and such that pq is nearly perpendicular to bd. The images of pq and pr appear to the observer, O, in the direction afg. Further adjustments should be made at this point upon C, H and Q, so that these images stand out clearly and brightly. Various parts of these images may be superposed by tilting H and C. In Fig. 2 this is also accomplished by moving either C or H along the line bf. When any obstacle containing a pinhole in it is now placed between the source of light, S, and A, four images of this pinhole are seen by the observer along afg. If A, C and H, have been more than half silvered, the two brightest of these images are those due to reflection from the half silvered surfaces. When these brightest pinhole images are superposed by tilting Q, fringes are invariably seen at once provided the differences in the optical paths abd and afe is not too great. Further adjustments may be necessary to improve the appearance of the interference fringes. This interferometer is designated as II (4). Interference fringes between D and pq are next formed by closing S_3, opening S_1 and S_2, and adjusting D alone. In this adjustment the paths bc and bd should first be made approximately equal. The pinhole images may then be superposed as in the preceding case. This interferometer is denoted as II (5). Similarly, by closing S_1, opening S_3 and S_4, and adjusting I alone, interference fringes between I and pr are formed in the interferometer denoted as II (6).

The problem of photographing the above interference patterns is not as simple as might be suspected. A broad, monochromatic source of light and a condensing lens are necessary to secure uniform illumination and fringes with good visibility. A long focus camera is preferable to one of short focal length. In the operation of securing a good image of the interference pattern on the ground glass of the camera it is ordinarily not sufficient to adjust the camera alone. The image on the ground glass can be greatly improved by decreasing or increasing either abd or afe. The white light position is not always to be preferred and need not, therefore, be secured. The condition of the half silvered surfaces is much

more critical in the photographic work than in that of observing by eye. The evaporation method[3] is highly recommended for half silvering.

The skeleton parts of interferometers II (4), II (5) and II (6), are arranged in Fig. 3, with

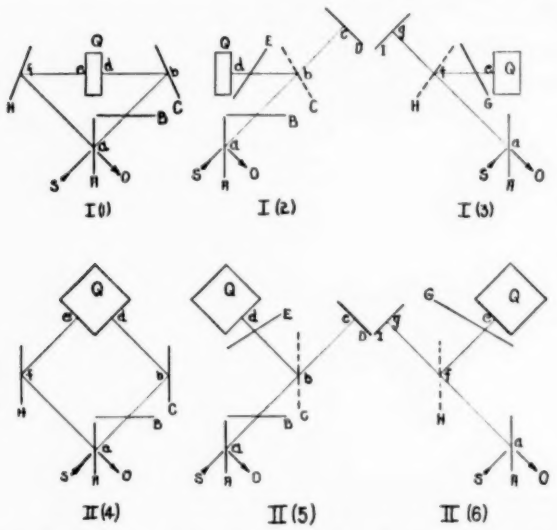

FIG. 3. Skeleton parts of various interferometer arrangements.

those of I (1), I (2) and I (3), to bring out more clearly the essential working parts and differences in these interferometers.

Suppose that in adjusting II (4) the images of *pq* and *pr*, Fig. 2, are superposed in such a way that the particles whose relative motion is indicated by the arrows *l* and *k* are brought into coincidence. For relative motions of the type indicated by *l* and *k*, II (4) will in general indicate smaller amplitudes of vibration than either II (5) or II (6) since in II(4) both optical paths *db* or *ef* are lengthened or shortened simultaneously. On the other hand, for relative motions of the type *n*, *m*, II (4) will always show larger amplitudes of vibration than either II (5) or II (6). The amplitudes in II (4), II (5) and II (6), may be compared in rapid succession with the aid of the shutters.

For descriptions and figures of the mechanical parts of the triple interferometer in Fig. 1, the reader should refer to the earlier paper.[4] The crystal, *Q*, and the dividing mirrors *C* and *H* are mounted upon separate carriage blocks which may be moved on a common track along the line *bdef*. The crystal carriage block was provided with guides by means of which the crystal mounting can be moved along the line *MN*, Fig. 2. These guides are very convenient in shifting from optical arrangement *I* to optical arrangement II. It is necessary only to move the crystal mounting in the direction *MN*, turn the crystal through an angle of 45°, and rotate *H* and *C* into parallelism with *A*.

The multiple interferometer is not limited in application to the rectangular plate. The angle between opposite or adjacent faces may vary quite widely since the beams *bd* and *ef* can be returned to *A* for interference by adjusting the dividing mirrors properly with respect to *Q*.

CRYSTAL PLATES

The multiple interferometer will be illustrated by a group of observations upon two interesting patterns appearing in square plates of *X*-cut. These patterns have previously been studied in both square and circular plates with the aid of a dust and mechanical method by R. B. Wright and D. M. Stuart, who in Fig. 10 of their publication[5] refer to these patterns as *A* and *B*.

The seven square plates are described in Table I in accordance with the terminology suggested by W. G. Cady[6] and followed by the writer.[7] The frequencies of *A* and *B* are listed as

TABLE I.

Crystal plate	Cut	*x* (mm)	*y* (mm)	*z* (mm)	Direction of electric field	*nA*	*nB*
1	*X*	7.867	35.984	35.979	X	66.5	83.3
2	*X*	8.069	36.017	36.020	X	66.25	83.2
3	*X*	4.745	36.017	36.020	X	66.3	83.25
4	*X*	4.745	32.108	32.113	X	74.37	93.25
5	*X*	4.745	27.783	27.783	X	86.24	107.5
6	*X*	4.745	27.719	27.716	X	86.27	107.6
7	*X* or *Y*	10.381	10.382	10.385	X	209.4	——
8 Wright and Stuart	*X*	4.810	36.02	35.98	X	66.8	83.6

Plate 7 is a cube and can therefore be used as an *x*, *y* or *z*-cut.

[3] C. H. Cartwright and J. Strong, R. S. I. **2**, 189 (1931).
[4] H. Osterberg, J.O.S.A. **23**, 34 (1933).
[5] R. B. Wright and D. M. Stuart, Bur. Standards J. Research **7**, 519 (1931).
[6] W. G. Cady, P.I.R.E. **18**, 2136 (1930).
[7] H. Osterberg, J.O.S.A. **22**, 28 (1932).

nA and *nB* in kilocycles/sec., and are compared with those observed by Wright and Stuart. These plates have been both cut and plane polished by the writer. Opposite sides are parallel to about 0.001 mm. Adjacent sides are perpendicular to the limit attainable with a good square. The orientation of the plate with respect to its crystallographic axes is accurate to at least one-fourth degree. All plates were cut from the same crystal of Brazilian quartz, which was of good optical quality. Plates 3 to 6 were cut down from plate 2. The crystals were driven by an electric field applied along *X*, the electric axis, through strips connected to the variable condenser of a Hartley oscillator. These strips are often apparent on the photographs. The surfaces under observation were usually silvered.

Pattern A

Pattern A, which appears at *nA*, the lower frequency, Table I, is described in Fig. 4, with the aid of photographs of the various interference patterns from crystal 6. Corresponding photographs from the other crystals are identical in appearance.

To gain facility in interpreting the interference patterns, the reader should study the mathematical analysis of an earlier paper.[8] It should be borne in mind that when amplitudes of vibration are mentioned throughout the following discussion, these are actually the components of vibration along the normal to the particular surface under observation.

Fig. 4, A, represents the fringe appearance on both major surfaces in interferometers I (2), I (3), II (5) and II (6). The original fringes, almost undisturbed, appear on the corners *a*, *b*, *c*, *d*, which are nearly at rest. The narrow ring of the outer elliptical figure extends over that portion of the major surface whose amplitude is such as to obliterate the original fringes. Within this elliptical ring the amplitude is greater than the above value and reconstructs a set of fringes whose brightness maxima are shifted by one-half fringe width. A continuous increase in the amplitude of vibration results in alternate destruction and reconstruction of the fringes. Each reconstruction is accompanied by a shift of one-half fringe width and results in poorer contrast than in the preceding fringes. A second obliteration surrounds the middle of the major surface. Within this smaller ring of obliteration the greatest amplitudes, sufficient to cause a second reconstruction, are reached.

Fig. 4, F, represents the fringe pattern in I (1) at all amplitudes. No fringe disturbance is seen in this interferometer whereas large fringe disturbances occur in I (2), and I (3). The relative motion of opposing particles on the major surfaces is therefore that indicated by arrows *k* and *l*, Fig. 1. Pattern A, it appears, is compressional in nature.

Lycopodium powder settled temporarily along the white dotted line at an angle of $-21.4°$ with the optic axis, which is parallel to the edge *db*.

Fig. 4, D, is photographed from the face *db* in I (2). A node is clearly visible near *b*. The amplitude is very great over a region to the right of *d* in which it is a maximum. This region can be distinguished at smaller amplitudes of vibration. The pattern from *ac* in I (3) is so symmetrical with the above pattern that no photograph was taken. It is illustrated by Fig. 4, B, in which the node is present near *c*. In the case of crystal 1 the maximum amplitude of oscillation on *bd* or *ac* was sufficient to produce the fifteenth blurring of the fringes. This amplitude is equal to 3.69 wavelengths of the green light used for illumination (5461A). Fig. 4, J, was photographed from I (1) in which the reflecting faces were *bd* and *ac*. From the presence of the node near the middle of this photograph and a comparison with photographs B and D, one concludes that near the middle of faces *bd* and *ac* opposing particles move relatively as indicated by *k* and *l*, Fig. 1.

The fringe appearance on *ab* and *dc* in I (2) and I (3), respectively, is shown in Figs. 4, C and E. These patterns are, again, symmetrical. The nodes occur near the middle of the surfaces. In photographing C the crystal was made to vibrate with less amplitude than in D for the purpose of showing more clearly *m*, the region of greatest amplitude. The pattern Fig. 4, L, was formed in I (1) by reflection from *ab* and *cd*. Its similarity to Fig. 4, J, is striking. Opposing particles on the middle of *ab* and *cd* thus move relatively as indicated by *k* and *l*, Fig. 1. Since particles in the same surface located on opposite sides of a node move

[8] H. Osterberg, J.O.S.A. **22**, 20 (1932).

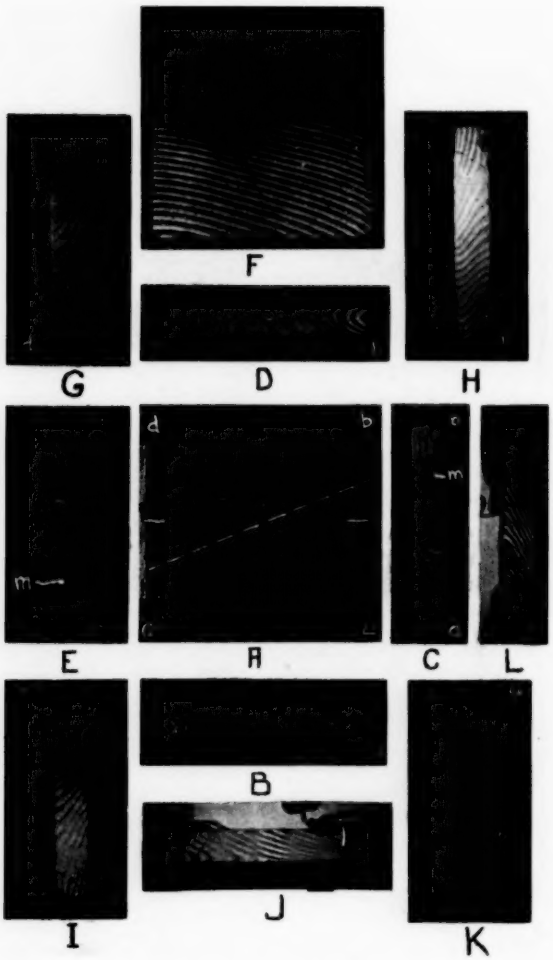

FIG. 4. Photographs of various interference patterns from crystal 6, pattern A.

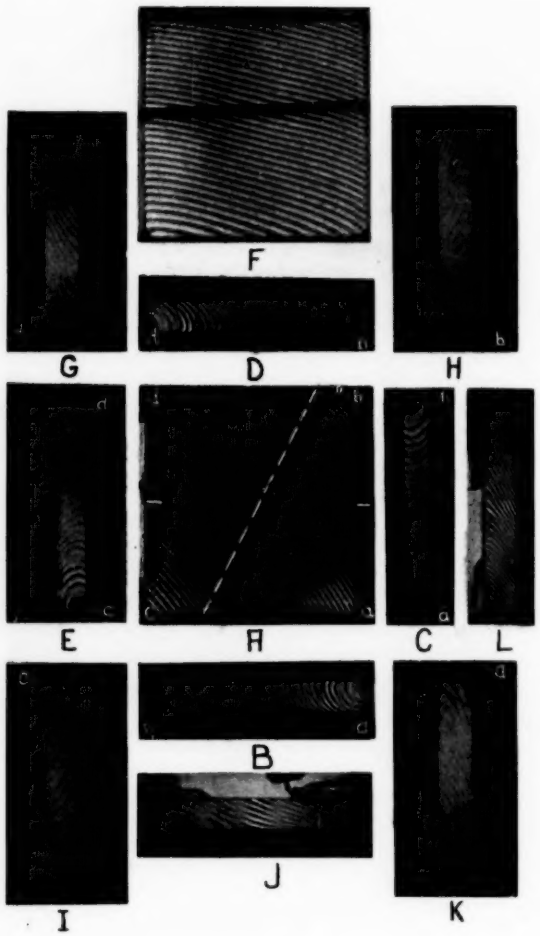

FIG. 5. Photographs of various interference patterns from crystal 6, pattern B.

opposite in direction, it follows that with the simple observations in the above paragraphs the relative direction of motion of the opposite surfaces is known. Figs. 4, G, H, I and K, are formed in II (4) by reflection from two perpendicular faces as in Fig. 2. From Fig. 2 it is clear that in the case of a square plate it is most natural to superpose the images of r and q in adjusting for fringes. In Fig. 4, H, for example, db and ba are the reflecting faces of which the images of d and a are superposed. Corners b of H and b of A correspond. Figs. 4, G, I and K, bear a similar relation to A. One is immediately struck by the similarity of Figs. 4, G, H, I and K. In all cases the middle region suffers the greatest apparent amplitude and the amplitude is more uniform over the surface than in the other photographs. By comparing Figs. 4, C, D and H, it is evident that particles near a and d on the surfaces ab and db are moving relatively as indicated by k and l, Fig. 2. The same conclusion applies to the corresponding particles near a and d on the surfaces cd and ac by a similar comparison of Figs. 4, B, E and I. These facts enable one to picture the relative motion of the narrow faces of the crystal.

The relative motion of the two major faces with respect to the edge faces was determined in the following interesting manner. In II (4) an interference pattern very similar to Fig. 4, C was obtained by the superposition of the images of the face ab and a strip extending across the middle of one of the major surfaces, the particular major

surface being immaterial since their relative motion was known. The above strip was chosen since the middle part of the major face has the greatest amplitude and since even this amplitude is only about one-fourth of that of the edge faces. In crystal 2, for example, the node on Fig. 4, C, was located at a distance 22.0 mm from *b*. In the above interference pattern this node had suffered an apparent shift to a new position 20.3 mm from *b*. This showed definitely that particles on the major surface move relatively to those near *b* on *ab* as indicated by *k* and *l*, Fig. 2 and relatively to those near *a* on *ab* as indicated by *n* and *m*, Fig. 2.

The nodal lines present on the crystal edge faces, particularly those upon *ab* and *cd*, become very narrow with increased amplitude of vibration. It is interesting to compare these nodal lines with those of the dust pattern, Fig. 10, a, of the article by Wright and Stuart.[9] One is immediately impressed by the greater certainty and ease with which the optical phenomenon is interpreted. The optical patterns are also subject to being measured with the greater accuracy as, for example, with a long focus travelling microscope. From measurements made in this manner the angle, γ_1, between the optic axis and a line drawn in the plane of the plate through the nodes on *ab* and *cd* was found to be $14°\pm40'$. A similar line through the nodes on *bd* and *ac* makes an angle $\gamma_2=-52°$ with the optic axis.

The facts established in the preceding paragraphs regarding the type of vibration in pattern A are assembled in Fig. 6. Small arrows have been drawn across the edges to indicate their motion at the instant when the upper major surface is moving toward the reader. This major surface is that which becomes positive upon the application of pressure. The approximate relative amplitude of vibration of the edge faces is given, for example, at some point *C* by the length *BC*. The displacements along the small arrows appear to be components of two displacements described by the large arrows.

The dust line, *mn*, inclined $\gamma_2=-21.4°$ with the optic axis cuts the edge faces *ab* and *cd* in Fig. 4, A, in the region in which these faces have

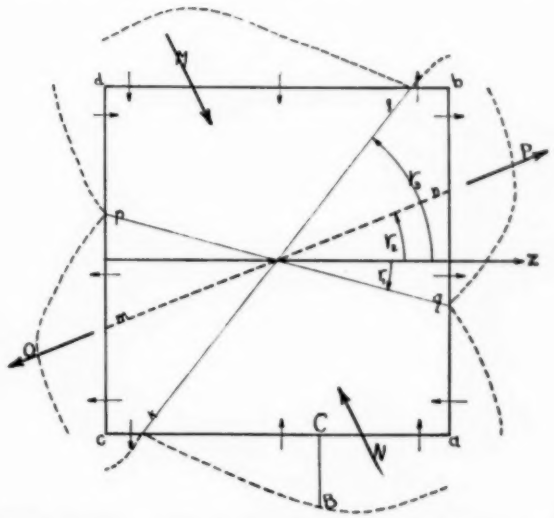

FIG. 6. Summary of facts regarding vibrations in pattern A.

the greatest amplitude. It appears to be a node in the plane of the plate for the compressional vibration along *MN*. The amplitude along *MN* is somewhat greater than that along *OP*. The above statements are consistent with the observation that lycopodium strewed upon the major surface first moves inward toward *mn* and outward along it. For consider the actual motion of a particle located within the area *acmn* in the upper major surface. By neglecting the component parallel to *mn*, this particle is subjected to two simple harmonic motions which are mutually perpendicular and whose phase relations are such that the upward component of motion is accompanied by a larger horizontal component parallel to *N*. The particle thus moves in an elliptical orbit with the proper velocity to impart to the dust particles with which it comes in contact momentum in the direction of *N*, i.e., toward *mn*. Contact with dust particles is made only when the particle is moving upward. Similarly, particles located in the area *bdmn* in the upper major surface move the dust particles toward *mn*. Particles located along *mn* in the upper surface are subjected to a horizontal component of vibration only along *mn*. The phase relations between the upward component and the horizontal component along this line is such as to move the dust outward from the center of the plate along the directions *O* and *P*.

In Fig. 7, following Wright and Stuart, Young's modulus in the plane of an *X*-cut is plotted as

[9] R. B. Wright and D. M. Stuart, Bur. Standards J. Research **7**, 519 (1931).

ordinates and γ, the angle between the optic axis and the direction in which Young's modulus is sought, as abscissas. The line *kl*, Fig. 6, corresponds closely to the direction in which Young's modulus is a maximum. Similarly, *pq* corresponds closely to the direction in which Young's modulus

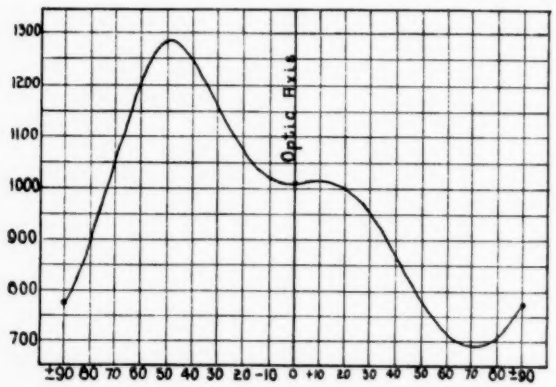

FIG. 7. Young's modulus in the *YZ* plane of an *X*-cut as given by Wright and Stuart. Young's modulus in kilomegabaryes as ordinates. γ in degrees as abscissas.

is a maximum on the other side of the optic axis. The direction *MN* is that in which Young's modulus is a minimum. Similar relationships regarding the lines through nodes of radial displacement are pointed out by Wright and Stuart in the case of a circular plate of *X*-cut, for which their method of probing the radial air currents can be depended to give quite accurate results.

Pattern A is compressional in nature, formed, without a doubt, by two sets of compressional wave trains propagated in opposite directions in the plane of the plate and incident at angles different from 90° upon the four crystal edges. These angles must be those which enable the wave trains to repeat their course periodically. Under such circumstances the critical values of Young's modulus are of importance in determining the particular form of those patterns for which periodicity is possible. In plates of either *X* or *Y*-cut the writer has found that one of the most common types of pattern is a regular and beautiful series due to the reflection of flexural wave trains at angles different from 90° upon the four sides of the plate. These flexural wave trains thus "circulate" within the plane of the plate in a manner similar to the compressional waves in pattern A.

PATTERN B

Pattern B is described in Fig. 5, in which the photographs from crystal 6 are arranged as in Fig. 4. The major surfaces show almost the same interference pattern and have the same relative motion in pattern B as in the case of pattern A. This is shown by Figs. 5, A and F. The vibration of the individual edge faces is quite different, as can be judged from Figs. 5, B, C, D and E. Opposite edge faces vibrate symmetrically, as in pattern A. The nodes on *ac* and *db* are very distinct. The faces *cd* and *ab* could be brought into motion as a whole by increasing the amplitude of vibration, the corners *b* and *c* vibrating with less amplitude than *a* or *d*. Lycopodium powder was found to move toward the dotted white line inclined at $-64°$ with the optic axis and then slide outward as in pattern A. This line cuts *bd* and *ac* in those regions where these faces have their greatest amplitude. Figs. 5, J and L, from I (1) indicate that at the middle of the edge faces opposing particles on either set of parallel edge faces move relatively as indicated by *k* and *l*, Fig. 1 and with equal amplitude. Figs. 5, G, H, K and I, from II (4), are strikingly similar. They show that particles from the middle of any two perpendicular edge faces move relatively as indicated by *m* and *n*, Fig. 2. These patterns, photographed with the crystal oscillating weakly, possess a more uniform amplitude of oscillation than the others.

In the pattern (not shown) formed in II (4) by reflection from *ac* and a strip across a major surface, the node present on *ac* in Fig. 5, B, suffered an apparent shift in the direction *a* to *c*. This showed that an outward motion of particles on *ac* located to the left of the node is accompanied by an upward motion of the major surface which faces the reader.

A line in the plane of the plate through the node on *ac* and on *bd* forms an angle of $57.5 \pm 1°$ with the optic axis. It does not coincide with any direction in which Young's modulus has any unusual features, Fig. 7.

Fig. 8 is a summary of the main facts regarding pattern B. The small arrows indicate the relative motion of the edges at the instant when the upper

major surface is going toward the reader. The approximate relative amplitude at a point C is given in terms of the length CD. The dust line, mn, forms an angle, $\gamma = -64 \pm 2°$ with the optic axis. The line pq through the nodes on bd and ac forms an angle of $57.5 \pm 1°$ with this axis. Par-

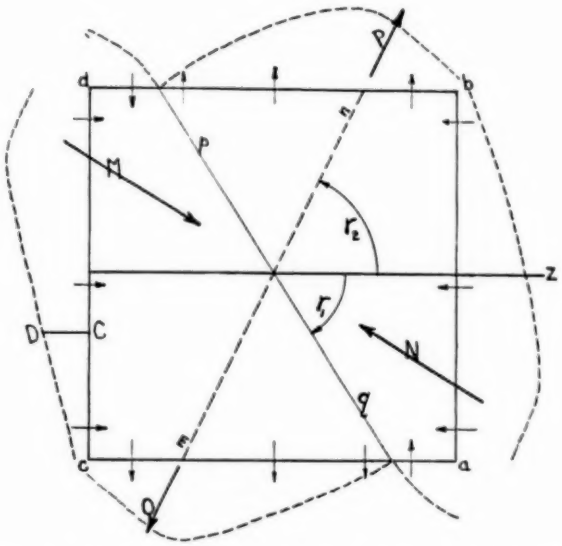

FIG. 8. Summary of facts regarding vibrations in pattern B.

ticles appear to enjoy the maximum displacement in the plane of the plate in the directions MN and OP, the larger amplitude being along MN. The dust node, mn, is most probably the node of vibrations in the plane of the plate along MN.

Pattern B, like pattern A, is compressional in nature and formed by two longitudinal wave trains propagated in opposite directions in the plane of the plate. These patterns differ in the very interesting respect that pattern A possesses two sets of radial nodes, determining kl and pq (Fig. 6), while pattern B has only one, determining pq, Fig. 8.

HUYGHEN'S CONSTRUCTION

The publication by Wright and Stuart of Young's modulus for the various directions in quartz plates is of great assistance in the application of Huyghen's construction to determine the relation between the angles of incidence and reflection of a compressional wave incident at any angle upon the boundaries of a quartz plate. The writer has not thus far succeeded, using this method of attack, in discovering which sets of compressional wave trains are those which form either pattern A or B. It is to be expected that though Huyghen's construction will enable one to discover the above wave trains, the actual position of the nodes will also be affected by the phase changes suffered by the waves upon reflection. The calculation of these phase changes for an anisotropic medium as a function of the angle of incidence is a pressing need.

Observations with the interferometer upon a large number of rectangular plates of X-cut and one circular plate of this cut have not revealed a single longitudinal pattern due to the reflection of compressional waves back and forth between any two opposite surfaces in the manner in which this phenomenon occurs in an open ended organ pipe. These observations, which apply to waves along X, Y or Z, are in direct contradiction with conclusions which, in the writer's opinion, have been drawn too freely in the past. The complexity, as regards variation of the amplitude of vibration over the crystal faces, of the mode whose frequency is, supposedly, determined by the thickness of the plate, has occasionally been mentioned.[10, 11] A recent publication by D. W. Dye[12] of some beautiful patterns from vibrating quartz plates contains no example of a pattern in which the two opposite reflecting end surfaces move even approximately as a whole.

It has been stated above that the coincidence of the observed and computed frequencies is a poor criterion for determining the type of vibration. The use of lycopodium powder for this purpose, particularly for plates of small area, is not reliable; for, many patterns which violently remove every trace of the applied powder show a regular set of nodes and antinodes upon this area when viewed simultaneously in the interferometer. The difficulties of interpreting even the simple dust figures of patterns A and B of this report have been discussed above. It is seriously to

[10] P. Vigoureux, *Quartz Resonators and Oscillators*, p. 58, 1931.

[11] S. Nishikawa, V. Sakisaka, I. Sumoto, Phys. Rev. **43**, 363 (1933).

[12] D. W. Dye, Proc. Roy. Soc. **A138**, 1 (1932).

be questioned whether it is necessary to carry out the customary method of edge grinding in order to facilitate the excitation of the fundamental longitudinal mode along X. By far the greatest number of patterns in the ordinary X-cut are due to flexural waves propagated in the plane of the plate. A much smaller number is due to longitudinal waves also propagated in the plane of the plate but incident (as in patterns A and B) at angles different from 90° upon the boundaries of the plate. For a given thickness of plate the effect of edge grinding is thus in general to increase the frequencies of these patterns. It is then a matter of coincidence, persistence, or experience to secure a pattern whose frequency approximates the desired frequency and whose major surfaces possess sufficient polarization for the purpose of frequency control.

It is reasonable to suppose that the fundamental longitudinal mode along the X direction in a quartz plate of X-cut cannot be excited (1) unless it is physically possible for a wave front, incident normally upon either of the two parallel reflecting end surfaces to retrace its course after each reflection from the same surface and (2) unless this wave front does not suffer appreciable damping. When these conditions are fulfilled, it then appears that at resonance the converse piezoelectric effect serves primarily as a means of supplying the energy required for sustained oscillations. If Huyghen's construction is used to describe the wave front after reflection, it will be found that the direction of propagation of the infinitesmal portions of the wave front is not parallel with the normal to the wave front. From Fig. 7, it is clear that this direction may form an angle of 40° with the normal, X, to the wave front. As a consequence, the wave front after reflection from either of the end faces will have sidled into the edges of the plate and there have suffered reflection before it is incident upon the second end surface. In the case of plates of large x dimension the entire wave front will have sidled into the edges of the plate. For such plates neither condition (1) nor (2) above is satisfied. It should be remembered that this situation differs considerably from the optical one in that the crystal dimensions, and therefore the wavelength, may be large as compared to the wave front.

Young's modulus in quartz assumes its extreme values in the YZ plane, for which Fig. 7, applies. Its maximum value is almost twice as great as its minimum value.

For specially oriented X-cuts in which the two reflecting end faces are ground perpendicular to the directions in which Young's modulus is a maximum (or, perhaps, a minimum) the direction of propagation of the infinitesimal portions of the reflected wave front is parallel with the normal to the wave front. For these cases conditions (1) and (2) are satisfied.

This phenomenon, which is fundamental to an understanding of the character of the longitudinal modes possible in an anisotropic solid, is being studied experimentally with some care and will be described in greater detail elsewhere.

Frequency-Dimensional Ratios of Patterns A and B

The frequencies of patterns A and B are very nearly independent of the thickness, x. This is shown in Table I by crystals 1, 2, 3 and 8, whose thicknesses vary, the lengths y or z being constant.

An analysis of the frequencies of crystals 3, 4, 5 and 6, in which the thickness is constant, shows that these frequencies are inversely proportional to the length y or z to an accuracy at least equal to that with which these frequencies can be determined with a General Radio Precision Wavemeter, that is, to an accuracy of about 0.25 percent. These facts are in accord with the supposition that patterns A and B are formed by two compressional wave trains circulating in the plane of the major surfaces.

Pattern A was formed on crystal 7 at 209.4 kc/sec. together with another pattern. The difficulty of keeping these two patterns separate accounts for a mistake in the article[13] on the triple interferometer. In this article crystal 7 is listed as crystal 14. The pattern at 210 kc is incorrectly concluded to be due to a simple longitudinal pattern propagated along X as in an open ended organ pipe, showing, as stated, a peculiar nodal belt on the faces perpendicular to Y and Z.

[13] H. Osterberg, J.O.S.A. **23**, 32 (1933).

Pattern A departs widely in this case from the frequency-length proportionality of the preceding paragraph. Its nodes are markedly curved at the smaller amplitudes of oscillation, suggesting end corrections or cross coupling.

Further regrinding of crystal 6 is obviously desirable.

The multiple interferometer is at present, however, being modified to determine the relative motion of all parts of a circular plate. A report on this experiment is forthcoming.

The writer takes pleasure in expressing his indebtedness to the National Research Council for a grant which has been of great assistance in the continuation of this work.

My thanks are also due to J. R. Roebuck for his helpful interest in the progress of this work and his criticism of the manuscript.

Successive Approximations by the Rayleigh-Ritz Variation Method

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(Received March 18, 1933)

Approximate eigenvalues given by the Rayleigh-Ritz variation method for handling linear differential equations are examined and relations are established between the discrete eigenvalues obtained in successive approximations. These relations should be of use in practical computations. A method for fixing upper bounds to eigenvalues is given and a procedure previously employed by the writer to simplify determinant calculations is adapted for use in the present theory.

THE variation method[1] of Rayleigh and Ritz has found frequent application in the determination of approximate solutions for differential equations arising in physical problems. Considerations of "eits" and "eifs" (Bateman's[2] useful abbreviations for "Eigenwerte" and "Eigenfunktionen") for excited wave mechanical systems have indicated that there are points which require study. This note is a result of such investigation. Certain aspects of the behavior of eits in successive approximations are examined here but no attempt is made to consider convergence or approximate eits for continuous ranges.

For definiteness our equations are summarized. A linear differential equation[3] in variables $x_1, x_2, \cdots, x_N$ is considered:

$$[H(x_1, \cdots, x_N, \partial/\partial x_1, \cdots, \partial/\partial x_N) - W_c]\Psi_c(x_1, \cdots, x_N) = 0 \equiv [H - W_c]\Psi_c = 0. \tag{1}$$

W_c is a correct eit associated with a correct eif Ψ_c. Corresponding approximations W_a and Ψ_a are given by the following equations:

$$\Psi_a = \sum_{n=1}^{m} c_n \Phi_n(x_1, \cdots, x_N), \tag{2}$$

$$\int \Psi_a^* \Psi_a d\tau = 1, \qquad \delta \int \Psi_a^* H \Psi_a d\tau = 0, \qquad \int \Psi_a^* H \Psi_a d\tau = W_a. \tag{3}$$

In these equations $\Phi_1, \cdots, \Phi_m$ are m linearly independent known functions which satisfy the boundary conditions.[3] The δ refers to a first variation applied to the c_n's. The volume element of the $x_1, \cdots, x_N$-space is $d\tau$. The assumed properties of H and of the Φ's give

$$H_{ij}\left(= \int \Phi_i^* H \Phi_j d\tau\right) = H_{ji}^*; \qquad \text{we shall use} \qquad \delta_{ij} = \int \Phi_i^* \Phi_j d\tau = \delta_{ji}^*.[4] \tag{4}$$

Eqs. (2), (3) and (4) give

[1] See: N. Kryloff, Mem. des Sci. Math. fasc. XLIX (1931); also, K. Hohenemser, *Die Methoden zur Angenaherten Losung von Eigenwertproblemen in der Elastokinetic*, pp. 27–30, Berlin, Springer, (1932); also, Kemble, Rev. Mod. Phys. **1**, 206 (1929).

[2] Bateman, *Partial Differential Equations of Mathematical Physics*, preface, Cambridge (1932).

[3] Self-adjointness is assumed together with quadratic integrability of the solutions concerned, and the vanishing of the "bilinear concommitant" on the boundary. See: E. L. Ince, *Ordinary Differential Equations*, p. 123, Longmans (1927); also H. Weyl, Math. Ann. **68**, 220 (1910).

[4] This $\delta_{ij} = \delta(i, j)_{=1}^{=0}{}_{i=j}^{i \neq j}$ if the Φ's form a normalized orthogonal set, otherwise $\delta_{ij} \neq \delta(i, j)$.

$$\int \Phi_i^*(H-W_a)\Psi_a d\tau = 0 = \sum_{j=1}^{m}(H_{ij}-W_a\delta_{ij})c_j, \quad i=1, 2, \cdots, m; \qquad \sum_{i=1}^{m}\sum_{j=1}^{m} c_i^*\delta_{ij}c_j = 1, \tag{5}$$

whence the m-rowed determinant

$$D_m(W_a) = \left(H_{ij}-W_a\delta_{ij}\right) = 0 \tag{6}$$

From (6) we may obtain the m real roots[5] $W_a = W_{m1}, W_{m2}, \cdots, W_{mm}$ with corresponding $\Psi_a = \Psi_{m1}, \Psi_{m2}, \cdots, \Psi_{mm}$. For the latter, $\Psi_{mk} = \sum_{n=1}^{m} c_{mk,n}\Phi_n$ where the c's are determined by (5) with $W_a = W_{mk}$.

It should be noted that the approximations $\Psi_{m1}, \cdots, \Psi_{mm}$, like the correct Ψ_a's, form an orthogonal set. This orthogonality follows from (4) and (5) thus:

$$\int \left[\Psi_{mi}^*(H-W_{mj})\Psi_{mj} - \Psi_{mj}(H-W_{mi})^*\Psi_{mi}^*\right]d\tau = 0 = (W_{mi}-W_{mj})\int \Psi_{mi}^*\Psi_{mj}d\tau$$

$$\therefore \quad \int \Psi_{mi}^*\Psi_{mj}d\tau = \delta(i,j) \quad i,j=1, 2, \cdots, m.^6 \tag{7}$$

The "next approximation" in which is included another independent function Φ_{m+1} will be considered now. For convenience $\Psi_{m1}, \cdots, \Psi_{mm}$ and Φ_{m+1} will be used as our independent functions. Φ_{m+1} is formed by the usual processes[7] to be normalized and orthogonal to $\Phi_1, \cdots, \Phi_m$. The new determinant analogous to (6) is

$$D_{m+1}(W_a) = \begin{vmatrix} W_{m1}-W_a, & 0, & \cdots, & 0, & h_1 \\ 0, & W_{m2}-W_a, & \cdots, & 0, & h_2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0, & 0, & \cdots, & W_{mm}-W_a, & h_m \\ h_1^*, & h_2^*, & \cdots, & h_m^*, & h_{m+1}-W_a \end{vmatrix} = G_{m+1}(W_a) - F_{m-1}(W_a) = 0. \tag{8}$$

In (8)

$$h_r = \int \Psi_{mr}^* H \Phi_{m+1} d\tau, \quad r=1, 2, \cdots, m; \qquad h_{m+1} = \int \Phi_{m+1}^* H \Phi_{m+1} d\tau;$$

$$G_{m+1}(W_a) = (h_{m+1}-W_a)\prod_{k=1}^{m}(W_{mk}-W_a); \qquad F_{m-1}(W_a) = \sum_{r=1}^{m}|h_r|^2 \prod_{k,\,k\neq r}^{m}(W_{mk}-W_a).$$

It is convenient to name the eits in increasing sequence thus: $W_a \equiv W_{m1} \leq W_{m2} \leq \cdots \leq W_{mm}$ for the "m-th approximation" eits pertaining to (6); also $W_a \equiv W_{m+1\,1} \leq W_{m+1\,2} \leq \cdots \leq W_{m+1\,m+1}$ for the "$(m+1)$-th approximation" eits pertaining to (8). To determine qualitatively the positions of the $(m+1)$-th relative to the m-th approximation eits consider the following:

$$D_{m+1}(W_{mr}) = -|h_r|^2 \prod_{k,\,k\neq r}^{m}(W_{mk}-W_{mr}) \quad \begin{matrix} \geq 0 \text{ if } r \text{ even}, \\ \leq 0 \text{ if } r \text{ odd} \end{matrix} \quad \text{since } (W_{mk}-W_{mr}) \quad \begin{matrix} \leq 0 \text{ if } k<r. \\ \geq 0 \text{ if } k>r. \end{matrix}$$

[5] Courant and Hilbert, *Mathematische Physik I*, p. 24, Springer (1931). See also Note (8).

[6] Strictly speaking suitable linear combinations of approximate eifs in a degenerate set must be made in order to have (7) hold within such a set.

[7] Whittaker and Watson, *Modern Analysis*, p. 224, Cambridge (1920). This procedure is, of course, only one of convenience and it will not affect the final results.

Also

$$D_{m+1}(W_a)\to\infty \quad \text{as} \quad W_a\to-\infty \quad \text{and} \quad D_{m+1}(W_a)\to(-)^{m+1}\infty \quad \text{as} \quad W_a\to\infty.$$

Therefore $D_{m+1}(W_a)$ must have at least one root between each succeeding two of the following W_a-values: $-\infty$, W_{m1}, W_{m2}, $\cdots$, W_{mm}, ∞. That there is *only one* root between each two follows from the fact that $D_{m+1}(W_a)$ can have only $m+1$ roots. Thus there is the rule:

(*1*) The m-th approximation eits separate those of the $(m+1)$-th approximation, i.e.,

$$W_{m+1\ 1}\leq W_{m1}\leq W_{m+2\ 2}\leq\cdots\leq W_{m+1\ m}\leq W_{mm}\leq W_{m+1\ m+1}.^{8}$$

Corollary 1.1 The p-th lowest eit, W_{mp}, of the m-th approximation is greater than (or equal to) the p-th lowest eit of any succeeding approximation, and therefore, assuming convergence of the process,[9] greater than (or equal to) the p-th lowest correct eit W_{cp}, i.e., $W_{mp}\geq W_{m+q\ p}\geq W_{cp}$ $q>0$.

It is "natural" to consider $W_{m+1\,1}$, $\cdots$, $W_{m+1\,s}$, $W_{m+1\,s+1}$, $W_{m+1\,s+2}$, $\cdots$, $W_{m+1\,m+1}$ as corresponding to[10] (or arising from) W_{m1}, $\cdots$, W_{ms}, h_{m+1}, $W_{m\,s+1}$, $\cdots$, W_{mm} respectively where h_{m+1} is greater than W_{ms} and (or)[11] less than $W_{m\,s+1}$. Then there is:

Corollary 1.2 Any m-th approximation eit which is {less/greater} than h_{m+1} $(=\int\Phi_{m+1}{}^{*}H\Phi_{m+1}d\tau$, Φ_{m+1} normalized and orthogonal to Φ_1, Φ_2, $\cdots$, $\Phi_m)$ is {greater/less} than its corresponding $(m+1)$-th approximation eit, i.e., $W_{m+1\ r}\leq W_{mr}r\leq s$ and $W_{m+1\ r+1}\geq W_{mr}r>s$. h_{m+1} "repels" eits.

(*2*) The eit $W_{m+1\ s+1}$ corresponding to h_{m+1} is such that $W_{m+1\ s+1}\gtreqless h_{m+1}$ if

$$(-)^{s}D_{m+1}(h_{m+1})\left[=\left(\sum_{r=1}^{s}-\sum_{r=s+1}^{m}\right)|h_r|^2\prod_{\substack{1\\k,\ k\neq r}}^{m}|(W_{mk}-h_{m+1})|\right]_{\leq 0}^{\geq 0}$$

since $(-)^{s}D_{m+1}(W_{ms})\geq 0\geq(-)^{s}D_{m+1}(W_{m\,s+1})$ and since $D_{m+1}(W_a)$ can have but one root between W_{ms} and $W_{m\,s+1}$.

Corollary 2.1 If $h_{m+1}\leq W_{m1}$ then $W_{m+1\ 1}\leq h_{m+1}$; or if $h_{m+1}\geq W_{mm}$ then $W_{m+1\ m+1}\geq h_{m+1}$.
Corollary 2.2 If $W_{mr}=W_{mr+1}$, $r=1, 2, \cdots$ or $m-1$ then $W_{m+1\ s}=h_{m+1}$.

Corollary 1.1 is perhaps the most important one from a practical viewpoint; to avoid its misuse the following must be realized clearly. If it is desired to fix an upper bound to the p-th lowest correct eit it is *sufficient* to use *at least* p independent functions in the variation process. This condition may be regarded as *necessary* when there is no *a priori* knowledge of the correct eifs—the usual situation in practice. For example, if a single normalized function Φ were used to determine an approximate eit $W_a=\int\Phi^{*}H\Phi d\tau$, then it would not *necessarily* follow that $W_a\geq W_{c2}$, although, of course, $W_a\geq W_{c1}$ would hold true. It is also not necessarily true that if $W_a=W_{cn}$,

[8] The writer wishes to thank Professor H. Bateman of Pasadena for drawing his attention to the fact that this theorem is equivalent to one already known in algebraic theory. The following references are relevant: Hermite, Comptes Rendus, **41** and "Ouvres," **1**, 479; Salmon, *Higher Algebra*, section 47; Burnside and Panton, *Theory of Equations*, Vol. 2, p. 65; C. W. Borchardt, J. de Math. (1) **12**, 50–67 (1847); a slightly more general theorem is given by Bateman, Bull. Am. Math. Soc. **18**, 179 (1912).

[9] Formally the difficulty of continuous ranges of eits may be avoided in the treatment of an eif associated with a discrete eit as follows: assume that the Φ's are chosen so that they ultimately form a complete enough set to give correct expansions for a smaller set (say, t members) of discrete, correct eifs. The Φ's will all be of the discrete type and some of them may be formed by integration over a range of their "eits." However it must be noted that of the eits determined finally by the use of these Φ's only t of them will be necessarily correct.

[10] Of course in such discontinuous operations as are used here correspondences are necessarily arbitrary. In a sense each approximate eit contains elements of all the correct eits.

[11] The "or" refers to the case $h_{m+1}>W_{mm}$ or $h_{m+1}<W_{m1}$. The possibility of $h_{m+1}=W_{ms}$ or $W_{m\,s+1}$ is not excluded.

$n>1$, then $\Psi_a=\Psi_{cn}$.[12] The necessity of using at least p functions to fix an upper bound for the p-th eit will lead often to determinants of five or more rows and columns. For such many-rowed determinants the calculation of the roots may be prohibitively long in actual cases unless simplified by determinant manipulation. A many-rowed form like Eq. (6) can be replaced by any one of a variety of few-rowed determinants and, in this way, the calculations for certain roots will probably be shortened. For example, a small group of μ members in our set $\Phi_1, \Phi_2, \cdots, \Phi_m$ may be "physically important" for a certain group of eits, which means usually that non-diagonal terms may be small compared with diagonal terms in the part of the m-rowed determinant bordering the μ-rowed "underdeterminant." The contributions of these terms for the eits concerned may be calculated by means of an adaptation of the perturbation method used in a previous paper by the writer.[13] Other methods may be suggested by the forms of particular determinants.

[12] This fact introduces the question of what is meant by "best approximation." If an approximate eit is defined by $W_a=\int\Psi_a^*H\Psi_a d\tau$, $\Psi_a=\Sigma_1^m c_n\Phi_n$ it is always possible (at least in theory) to choose c's and Φ's such that $W_a=W_{cn}$ although a variation process might not lead to a similar result for a given set of fundamental Φ's. The term "best approximation" must refer in the final analysis to the use to which the W_a and the Ψ_a will be put.

[13] J. K. L. MacDonald, Proc. Roy Soc. (London) **A138**, 187 (1932). For present use the reference's Eqs. (9) and (10) are replaced by our (2), (3) and (5). $\Sigma_{s=1}^{\mu}(H_{rs}+\epsilon_{rs}-W_a\delta_{rs})c_s=0$ $r=1, 2, \cdots, \mu$ is substituted for Eq. (15). $(H_{r\sigma}-W_a\delta_{r\sigma})$ and $(W_a\delta_{\sigma s}-H_{\sigma s})/(H_{\sigma\sigma}-W_a\delta_{\sigma\sigma})$ replace $W_{r\sigma}$ and $\Omega_{\sigma s}$ in Eq. (16) of the reference, and σ ranges from $\mu+1$ to m.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Azimuthal Asymmetry of the Cosmic Radiation

The theory of the motion of electrically charged particles in the magnetic field of the earth has been developed by Störmer[1] to account for auroral phenomena, and by Lemaitre and Vallarta[2] to explain the latitudinal variation[3, 4] of the intensity of the cosmic radiation. The theory predicts that rays from infinity of energy V volts will strike the surface of the earth at latitude λ only from those angles θ from the meridian plane for which

$$\sin\theta > k^2\cos\lambda/R^2 - 2k/R\cos\lambda \qquad (1)$$

TABLE I.

Angle from vert.		Total time T (min.)	Total counts C	Counting rate C/T	Number of data n	Probable error from residuals	Probable error from number of counts	West-East difference
Set A 35°	East	698	5195	7.44	14	0.063	0.069	0.47±0.097
Run 1	West	922	7299	7.91	14	0.059	0.063	=6.3%±1.3% of E
Set B 41°	East	755	3984	5.28	12	0.048	0.057	0.54±0.074
*Run 1	West	1334	7776	5.82	15	0.049	0.045	=10.2%±1.4% of E
Set A 45°	East	843	4442	5.27	19	0.072	0.053	0.54±0.087
Run 2	West	1086	6319	5.81	19	0.050	0.049	=10.2%±1.65% of E
Set B 25°	East	453	2593	5.72	14	0.056	0.074	−0.04±0.10
Run 2	West	714	4051	5.68	12	0.064	0.060	=0.7%±1.73% of E
Set A 55°	East	1070	3530	3.30	21	0.038	0.037	0.34±0.058
Run 3	West	1122	4092	3.64	21	0.043	0.038	=10.3%±1.75% of E
Set B 65°	East	1613	1747	1.08	26	0.020	0.018	0.06±0.029
Run 3	West	1533	1741	1.14	22	0.022	0.018	=5.5%±2.7% of E
Set A 75°	East	1659	1615	0.97	25	0.020	0.016	0.05±0.027
Run 4	West	1773	1804	1.02	22	0.019	0.016	=5.1%±2.8% of E
Set B 30°	East	874	4110	4.70	13	0.063	0.049	0.32±0.088
Run 4	West	767	3855	5.02	13	0.061	0.055	=6.8%±1.87% of E
Set B 30°	East	1086	5085	4.67	5	0.027	0.045	0.30±0.065
Run 5	West	1064	5298	4.97	5	0.030	0.047	=6.4%±1.4% of E
Set B 30°	East	1042	4942	4.74	17	0.055	0.046	0.53±0.080
Run 6	West	884	4655	5.27	18	0.058	0.053	=11.0%±1.7% of E
Set A 45°	East	1413	7464	5.28	19	0.040	0.041	N=S=W
Run 5	West	1451	8173	5.63	21	0.041	0.042	0.35±0.059
	North	1605	9029	5.63	22	0.040	0.032	=6.6%±1.1% of E
	South	1690	9510	5.63	22	0.050	0.039	
Set A 45°	SE	1324	7127	5.38	18	0.039	0.043	Difference is insignifi-
Run 6	NE	1373	7371	5.40	17	0.036	0.042	cant
Set B 50°	East	1192	2691	2.25	18	0.028	0.029	0.26±0.042
Run 7	West	1190	2988	2.51	20	0.021	0.031	=11.5%±1.9% of E

* This run is not to be compared with other runs of Set B.

where R and M are the radius and magnetic moment of the earth and $k^2=300\ M/V$. On the basis of the theory of Lemaitre and Vallarta this implies the existence of an azimuthal asymmetry in the intensity of the corpuscular component of the cosmic radiation in latitudes where the intensity is varying, and the sign of θ in (1) is such that positive rays should enter more abundantly from the west. As has been stated by Lemaitre and Vallarta, on the basis of the intensity measurements of Compton an azimuthal asymmetry should be detectable in latitudes between the equator and 34° geomagnetic and on the basis of Compton's own analysis of his data the greatest E–W differences should appear in latitudes between 20° and 30°.

With this prediction in mind measurements have been carried out in a tent on the flat roof of the Hotel Genéve in Mexico City at an elevation above sea level of 2250 meters and in geomagnetic latitude 29°N. Two independent sets of Geiger-Mueller counters were used, arranged as coincidence counting telescopes.[5] A summary of the data obtained during the first two weeks is contained in Table I. Each run consisted of a series of n counting periods in positions alternating between the azimuths indicated. Usually the order E W W E, etc., was maintained in order to prevent long time variations of sensitivity from favoring any one azimuth. Changes in position from one azimuth to the other were made by rotation about a vertical axis so that any possible difference between the measured and true angle was the same, independent of the azimuth. The probable error of the mean counting rate has been estimated from the internal consistency. A comparison of this value of the probable error with that calculated by statistical theory from the total number of counts in the run is an indication of the possible extent of instrumental variations.

The results seem conclusive in showing that the west intensity is greater than that of the east at angles between 30° and 65° from the zenith. Every run within this range of angles shows the effect and in some cases the E–W difference is more than six times the probable error. The results therefore accord with the Lemaitre-Vallarta theory and show that the principal corpuscular component of the cosmic radiation is *positively* charged. The disappearance of the E–W difference at angles below 65° is to be attributed to atmospheric absorption, and the rate of loss of energy which may be determined in this way is in fair agreement with the fact that no latitudinal variations of intensity occur outside of the ±34° equatorial belt.

Run 5A, including the four principal azimuths, indicates equal intensities in all but the east. Since the west value of this run is somewhat less than that of run 2A this result is somewhat questionable, but if it is correct, it would mean that the forbidden cone is sharply limited to the region below 15° to 30° east of the meridian. This result is to be predicted from the energy band deduced by Compton at $x_0=0.45$.

The Lemaitre-Vallarta theory also predicts a slight asymmetry about the E–W plane with a slightly greater intensity from the South in northern latitudes. Run 6A was made with the hope of detecting this asymmetry by comparing the NE and SE intensities at 45° from the zenith. The asymmetry for these directions proved to be too small to detect, although the measurements show that the intensity has an intermediate value in these directions.

These studies are being supported jointly by the Carnegie Corporation through the Department of Terrestrial Magnetism of the Carnegie Institution of Washington and by the Bartol Research Foundation of the Franklin Institute. Acknowledgment is made of the cooperation of Dr. E. C. Stevenson and of Mr. Lewis Fussell, Jr., in constructing the apparatus and particularly for the wholehearted cooperation of Professor M. S. Vallarta in making arrangements in Mexico and in assisting with the observations.

THOMAS H. JOHNSON

San Rafael,
Mexico,
April 11, 1933.

[1] Wien Harms, Handbuch für Experimental Physik **XXV**, 418, et seq.

[2] Lemaitre and Vallarta, Phys. Rev. **43**, 87 (1933).

[3] A. H. Compton, Phys. Rev. **43**, 387 (1933).

[4] J. Clay, Proc. Roy. Acad. (Amsterdam), December 17, 1932.

[5] Johnson and Street, J. Frank. Inst. **215**, 239 (1933).

A Positively Charged Component of Cosmic Rays

The relatively low intensity of cosmic rays at low geomagnetic latitudes, as recently found by our associated expeditions[1] and others,[2] indicates that a part of the cosmic rays consists of electrified particles. When interpreted in terms of Lemaitre and Vallarta's theory[3] of the deflection of electrified particles by the earth's magnetic field, these results indicate that at geomagnetic latitudes higher than about 45° the earth's magnetic field should not alter the direction of the incoming rays as observed at sea level. This is in accord with the sea-level observations of Johnson and Street,[4] which show a symmetrical East-West distribution. At the geomagnetic equator an analysis of our intensity-latitude curves suggests that most of the cosmic rays which are affected by the earth's magnetic field are too strongly deflected to reach the earth's surface. If this is correct, there should be but little asymmetry in the direction of approach of the cosmic rays near the equator. In an intermediate zone, however, where the intensity *vs.* latitude curve is steep, the rays that are being affected by

[1] A. H. Compton, Phys. Rev. **41**, 111 (1932); **43**, 387 (1933).

[2] J. Clay and H. P. Berlage, Naturwiss. **37**, 687 (1932).

[3] G. Lemaitre and M. S. Vallarta, Phys. Rev. **43**, 87 (1933).

[4] T. H. Johnson, J. Frank. Inst. **214**, 689 (1932).

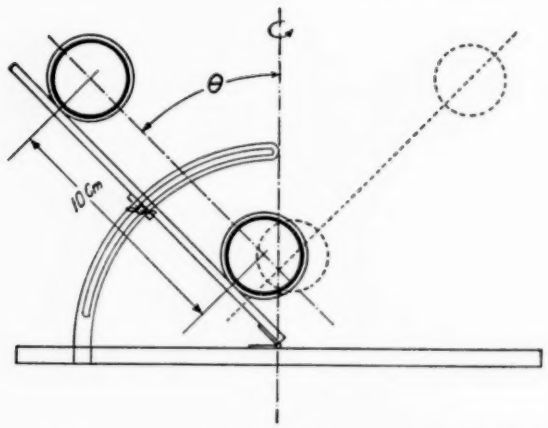

FIG. 1. Arrangement of coincidence counting tubes for studying East-West asymmetry of cosmic rays.

the earth's magnetic field should strike the earth from certain directions but not from others. If the rays are positively charged, they should come mostly from the west, if negatively, predominantly from the east, due to deflection by the earth's magnetic field. From such considerations Vallarta has suggested that Mexico City should be a good place to search for the predicted asymmetry in the direction of the incoming cosmic rays. Besides being in the favorable zone of geomagnetic latitude (29°N), its elevation (2310 meters) is sufficient to avoid some of the disturbing effects of the atmosphere.

In order to observe the direction of the incoming particles we have used a double coincidence counter, as shown diagrammatically in Figs. 1 and 2. Tests made by separating the tubes indicate that chance coincidences occur at the rate of only about 1.5 per hour, so that with a normal counting rate of about 5 per minute these were of negligible importance. The zenith angle θ of the line joining the axes of the tubes with the vertical was measured with the help of a protractor and spirit level. In order to avoid any possible change of conditions, the whole apparatus was mounted on a platform, which was rotated through 180 degrees when the changes between east and west were made. Readings of about a half hour's duration were taken alternately between east and west at the same zenith angle θ. For each angle the final series of readings totaled about fourteen hours on either side. By changing thus back and forth, enough readings were obtained to make a good estimate of the probable errors of the observed counting rates. The errors thus estimated from the consistency of successive readings under similar conditions were but little greater than those calculated as the statistical error from the total number of coincidences in the series. This means that no serious disturbing factor was affecting the readings. Table I summarizes our results.

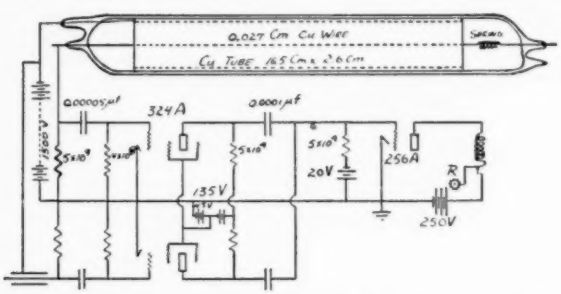

FIG. 2. Circuit used with double coincidence counter.

TABLE I. *East-west measurements at Mexico City, April, 1933.*

Geomagnetic latitude 29°N, elevation 2310 m, barometer, 56.5 cm.

Zenith angle		West	East	West/East
15°	Counts	5370	4856	
	Rate	6.83±0.07	6.64±0.07	1.03±0.02
30°	Counts	4897	4869	
	Rate	5.79±0.06	5.49±0.06	1.055±0.015
45°	Counts	2691	2693	
	Rate	3.70±0.05	3.30±0.05	1.12±0.02

It will be noted that at the larger zenith angles the rate at which the rays come from the west is greater than that from the east by several times the probable error of the measurements. It would appear that the asymmetry thus observed at Mexico City is considerably larger and more definite than that found by Johnson and Street[5] on Mt. Washington, geomagnetic latitude 55°N, elevation 1920 meters. This preponderance of rays from the west seems necessarily to imply the existence of a positively charged component of the cosmic rays.

Since our earlier measurements have shown that the cosmic rays at geomagnetic latitude 29° differ by only about 14 percent from those in high latitudes for this elevation, the difference in counts in the east and west directions is of the order of magnitude to be expected due to the deflection of the particles by the earth's magnetic field. The smallness of the effect confirms our earlier conclusion that most of the rays capable of penetrating the earth's atmosphere are not sufficiently bent by the earth's magnetic field to prevent them from reaching the earth. We may add that these data are consistent with the view that the positively charged component here found consists of Anderson's newly discovered[6] positrons.

We wish to thank Professor R. D. Bennett for suggesting the circuit used, Dr. M. S. Vallarta and Dr. T. H. Johnson for valuable suggestions in carrying on the experiment, and the Carnegie Institution of Washington for financial aid.

LUIS ALVAREZ
ARTHUR H. COMPTON

University of Chicago,
April 22, 1933.

[5] T. H. Johnson and J. C. Street, Phys. Rev. **43**, 381 (1933).

[6] C. D. Anderson, Science **76**, 238 (1932); Phys. Rev. **43**, 491 (1933).

The Production of X-Rays by Fast Mercury Ions

The production of soft x-rays (of the order of 2500 volts) has been observed when high-speed mercury ions strike targets of aluminum, sulfur, molybdenum, silver, tin and lead. The mercury ions used were accelerated to energies as great as 2.4×10^6 electron-volts by the method of Sloan and Lawrence,[1] with the improvements briefly described previously.[2]

The absorption of the radiation in aluminum was found to be exponential over a range of intensities extending down to about ten percent of the original value. There was no evidence of a continuous range of wave-lengths, although such a possibility could not be completely excluded by the absorption measurements. The wave-length of the radiation was determined from the absorption coefficients as measured in aluminum, mica and air. The results for the three absorbers are in quite good agreement, which shows that the radiation does not consist of particles of any sort, but must consist actually of x-rays. That the x-rays are due to the mercury ions and not to electrons was shown by several quite conclusive experiments.

In the case of the lighter targets used, the wave-length observed is in agreement with that of the *K*-series for the target in question within the accuracy of the absorption measurements. The intensity of the radiation from sulfur was about half that obtained from aluminum. One might expect such a result, since the sulfur *K*-radiation requires more excitation energy than does the aluminum *K*-radiation. The *K*-radiation from copper requires even more excitation energy (about 8000 volts) and this fact may explain why no measurable intensity of x-rays could be observed from a copper target. The *L*-radiation from copper would have been absorbed by the window separating the target from the ionization chamber.

In the case of the heavier targets used the wave-length of the radiation seems not to be characteristic of the target but rather of the mercury itself. Each of the targets (Mo, Ag, Sn, Pb) gave x-rays having a wave-length approximately that to be expected for the mercury *M*-radiation. In every case the excitation of the *L*-radiation of the target would have involved as much or more energy than the excitation of the mercury *M*-radiation. The greatest intensity was obtained from lead, and less from the others in the order: silver, tin, molybdenum.

Preliminary measurements have been made in order to determine the form of the excitation curve; i.e., the x-ray intensity as a function of the mercury ion energy has been observed. When the mercury ion current is of the order of 10^{-9} of an ampere, a measurable intensity is first observed in the case of silver and lead at energies of about 300 kilovolts. As the energy of the ions is increased the intensity rises rapidly. In the case of silver the intensity at one million volts is about ten times as great as when first observed and nearly sixty times as great at 2.3 million volts. In the case of lead the intensity at one million volts is nearly twenty times as great as at first, and about seventy times as great at 1.6 million volts. With molybdenum, the intensity first becomes measurable at about 800 kilovolts. At one million volts the intensity has doubled and at 2.3 million volts it is over fifty times as great as at first. There is no definite indication of saturation as far as the measurements were carried. There was also no evidence for a change in the wave-length of the x-rays with the energy of the ions.

A rough estimate of the efficiency of the process has been made. If it is assumed that the x-rays are emitted uniformly in all directions, calculations based on the results obtained show that at least one in every 2000 mercury ions having an energy of 2.3×10^6 electron-volts which strike a silver target succeeds in producing a 2400 volt quantum. This value probably represents a lower limit for several reasons, especially since the ionization chamber is probably not one hundred percent efficient in absorbing the x-rays, and because no corrections were made for absorption of the radiation in the target or for internal conversion of the quanta in the atom in which they are excited. The result may be compared with the value given by Bothe and Fränz[3] for the excitation of aluminum *K*-radiation by α-particles. They find an efficiency of 0.056 or about one in eighteen.

The author desires to express his gratitude to Professor E. O. Lawrence, under whose direction the work was done, for his continual interest and many valuable suggestions. It was at his suggestion that a search for x-rays produced in the manner described was first undertaken. The author is also indebted to Mr. David H. Sloan for advice in connection with the production of the high-speed ions.

WESLEY M. COATES

Radiation Laboratory,
Department of Physics,
University of California,
April 22, 1933.

[1] Sloan and Lawrence, Phys. Rev. **38**, 2021 (1931).
[2] Coates and Sloan, Phys. Rev. **43**, 212 (1933).
[3] Bothe und Fränz, Zeits. f. Physik **52**, 466 (1928).

The Spin of Hydrogen Isotope

For the further development of theories of nuclear structure it is very important to find the nuclear spins of the lighter atoms and especially of H^2. We have observed the emission spectrum of molecular hydrogen containing about 25 percent H^1H^1, 50 percent H^1H^2 and 25 percent H^2H^2, in the first order of a twenty-one foot grating which was kindly placed at our disposal by the Department of Physics. Seven of the alpha-bands of H^2H^2, with *P*, *Q*, and *R*-branches, have been examined. The *Q*-branches are strong and the relative intensity of their lines is being investigated. In all cases the transitions involving even rotational levels are more intense than those involving the odd. This shows at once that the spin of H^2 is neither zero, 1/2 nor 3/2. It may be stated without reasonable doubt that this spin is 2/2, or twice the spin of H^1.

GILBERT N. LEWIS
MURIEL F. ASHLEY

University of California,
May 3, 1933.

The Effective Neutron Collision Radius

The accurate measurements of Dunning and Pegram[1] of the transmission coefficients for neutrons of ten elements from carbon to lead show only a slow variation of total scattering per atom with atomic weight. One must therefore conclude (a) that the nucleus is the chief agent in scattering and (b) that the interaction function is not chiefly that of a polarized or polarizable particle in the field of a charge Ze. It seems more likely that the interaction is negligible until the approach is close and then rises very sharply. Such collisions are approximated by collisions between rigid spheres. Since the wave-length of the incident neutrons is of the order of magnitude of the radius of the nucleus (10^{-12} cm) one must use wave mechanics. In fact a classical calculation would yield less than one-third of the scattering for a given collision radius in this region. The solution[2] for the scattered wave is given by

$$\psi = -iC\sum_{n=0}^{\infty}(2n+1)\frac{F_n(kR)}{G_n(kR)}P_n(\cos\theta)\frac{e^{-ikr}}{kr}, \qquad (1)$$

where $k=2\pi mV/h=2\pi/\lambda$, $R=$nuclear radius$+$neutron radius, $F_n(kR)=(\pi kR/2)^{\frac{1}{2}}J_{n+\frac{1}{2}}(kR)$, $G_n(kR)=(\pi/2kR)^{\frac{1}{2}}\times H^{(2)}{}_{n+\frac{1}{2}}(kR)$, $J_{n+\frac{1}{2}}$ is a Bessel function and $H^{(2)}{}_{n+\frac{1}{2}}$ is a Hankel function of the second kind, $P_n(\cos\theta)$ is a Lagrange polynomial. This solution was first published by Mizushima.[2] The identical result was obtained by the late Dr. Gronwall of Columbia University and the values of $|\psi|^2k^2r^2/C^2$ for values of kR from 0.1 to 10 in intervals of 5° were tabulated by Mr. Taffel about two years ago. It is these tables that are used in this calculation.

The cross section per atom for scattering into a solid angle $d\omega$ is,

$$d\Phi=|\psi|^2r^2d\omega/C^2. \qquad (2)$$

Since the scattering experiments were performed after the neutrons had been filtered through 4 cm of lead it was assumed that all had the same velocity 35×10^8 cm/sec.[3] Φ is not very sensitive to small changes in velocity. The nuclear radius was assumed proportional to the cube root of the atomic weight (close packing) and for lead we use Gamow's value of 7.8×10^{-13} for the idealized core of the nucleus. The experimental value of the effective collision cross-section area is given by $1/\lambda N$ where N is the number of nuclei per cc of the scatterer and λ is the mean free path obtained from $p=e^{-d/\lambda}$ where p is the fraction transmitted and d is the thickness of the scatterer. Because of the finite size of the scatterer and the ionization chamber, this expression must be corrected since a considerable fraction of the singly scattered neutrons can enter the ionization chamber. The correction is made from Eq. (2) and varies from element to element. It amounts to 27 percent in lead and 9 percent in carbon. From the experimental value of the effective collision area we obtain R from Eq. (2) and by subtraction of the radius of the nucleus we obtain a neutron radius. The results are given in the table.

Element:	C	Al	S	Fe	Cu	Zn	Sn	I	Hg	Pb
Neutron radius ($\times10^{13}$):	1.45	1.37	1.24	1.15	1.33	1.15	1.54	1.08	1.33	1.43.

The average value is 1.31×10^{-13} and the experimental error amounts to ±0.2. It will be observed from the table that there is no progressive change of neutron radius with atomic weight, the variations are haphazard and within the limit of error. The scattering function $d\Phi$ seems to be in agreement with the preliminary results of Dunning and Pegram on large angle scattering in the case of carbon. The others could not be calculated from the data available.

The writer wishes to thank Messrs. Dunning and Pegram for putting their complete data at his disposal before publication.

I. I. Rabi

Columbia University,
May 3, 1933.

[1] Dunning and Pegram, Phys. Rev. **43**, 497 (1933).

[2] Mizushima, Phys. Zeits. **32**, 798 (1931).

[3] Curie, Joliot and Savel, Comptes Rendus **194**, 2208 (1932). Feather, Proc. Roy. Soc. **A136**, 709 (1932).

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